Projection of plane-wave calculations into atomic orbitals

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The projection of the eigenfunctions obtained in standard plane-wave first-principle electronic-structure calculations into atomic-orbital basis sets is proposed as a formal and practical link between the methods based on plane waves and the ones based on atomic orbitals. Given a candidate atomic basis, (i) its quality is evaluated by its projection into the plane-wave eigenfunctions, (ii) it is optimized by maximizing that projection, (iii) the associated tight-binding Hamiltonian and energy bands are obtained, and (iv) population analysis is performed in a natural way. The proposed method replaces the traditional trial-and-error procedures of finding appropriate atomic bases and the fitting of bands to obtain tight-binding Hamiltonians. Test calculations of some zincblende semiconductors are presented.

Keywords: D. electronic band structure; A. semiconductors

Plane waves and atomic orbitals provide two widely used methods for electronic structure calculations, each of them showing advantages and disadvantages. This paper proposes a way to use the advantages of each method to complement the other.

On one hand, plane waves (PW), in addition to \textit{ab initio} pseudopotentials, provide a very successful scheme to calculate the ground state properties of a large number of systems giving accurate results for electron densities, total energies, atomic forces, geometries, and energy bands. The origin of its wide applicability is the flexibility, simplicity, and accuracy of the plane-wave basis set: it has a homogeneous and universal completeness controlled by a single parameter, the energy cut-off. It is a floating basis, independent of atomic positions, and this greatly facilitates the calculation of atomic forces. Being equally complete everywhere, however, makes the PW basis inefficient, requiring a relatively large basis size for a given accuracy. In addition, plane waves require periodic boundary conditions. When the system is not periodic (molecules, surfaces, defects) such a periodicity must be imposed artificially by the use of supercells, which further increases the inefficiency of the basis.

On the other hand, methods based on the linear combination of atomic orbitals (LCAO) are far more efficient in terms of basis size, since atomic orbitals are much better suited to represent the molecular or Bloch wavefunctions. In addition, LCAO bases have recently experienced a renewed interest because of their suitability for order-N methods in which computational effort scales linearly with system size. Local bases also offer a natural way of quantifying magnitudes like atomic charge, orbital population, bond charge, charge transfer, etc., through population analysis. These quantities are essential for the chemical analysis of a condensed matter system since most of the chemical language is based on them. They provide a deep physical insight.

The price to be paid for the advantages mentioned above is the greater difficulty in the choice of the LCAO basis: since the results of calculations are affected by the election of the basis, a testing of the completeness and quality of the basis is critical. This task is much worse defined than in the case of plane waves since there are many more parameters than just a plane-wave energy cutoff, and usually ends up in a very cumbersome and non systematic trial-and-error procedure.

Thus, due to the difficulties and ambiguities of the LCAO basis construction and their less well controlled completeness, they are frequently considered more approximate than plane waves, and they have been traditionally used in less accurate tight-binding type of calculations. However, once a well optimized LCAO basis has been obtained, there is no reason why highly accurate \textit{ab initio} calculations cannot be performed with it. This raises the question of whether plane-wave calculations can be used to find an optimal or near-optimal LCAO basis, which can then be used in more complex situations while keeping a feasible computational effort.

Atomic orbitals constitute non-orthogonal basis sets in molecules and solids. Even though this kind of bases are more cumbersome to handle than orthogonal ones, they have shown to be more transferable and less environment-dependent, and to have a shorter range of interactions, being thus more adequate for non-parametrized LCAO methods. Non-orthogonalized atomic basis sets are therefore used throughout this work.

Most schemes proposed to optimize LCAO local bases are based on two procedures: (i) the minimization of total energies in atoms, molecules, or solids, and (ii) the optimization of energy bands as compared with experiments or with plane-wave calculations. In contrast, the present work links the plane-wave and LCAO methods by projecting the eigenstates of a plane-wave calculation into the Hilbert space spanned by the atomic basis. This provides an efficient and practical analytical tool which is applied to (i) characterize and optimize atomic basis sets, (ii) obtain LCAO bands and Hamiltonians, and (iii) analyze electronic structures by means of population analysis.

In this work the reference plane-wave calculations are...
performed within the local density approximation (LDA) for electron exchange and correlation using pseudopotentials that replace core electrons. These approximations are, however, not essential to the method. They can be replaced by others at will, the only key factor being the expansion of the one-particle wave functions in plane waves. The theory presented in this paper considers the PW results for the system of interest, and given the set of Hamiltonian eigenstates to be considered for the projection, the quality of an atomic basis is quantified by its ability to represent those eigenstates, i.e., by measuring how much of the subspace of the Hamiltonian eigenstates falls outside the subspace spanned by the atomic basis. For that we define the spilling parameter $S$

$$S = \frac{1}{N_k N_\alpha} \sum_{k} \sum_{\alpha=1}^{N_\alpha} \langle \psi_{\alpha}(k) \rangle \langle 1 - P(k) \rangle \langle \psi_{\alpha}(k) \rangle$$  \hspace{1cm} (1)$$

where $|\psi_{\alpha}(k)\rangle$ are the PW calculated eigenstates, and $N_k$ and $N_\alpha$ are the number of calculated $k$ points in the Brillouin zone and the number of bands considered, respectively. $P(k)$ is the projector operator into the subspace of Bloch functions of wave vector $k$, generated by the atomic basis, and defined as usual for non-orthogonal basis $P(k) = \sum_\mu |\phi_{\mu}(k)\rangle \langle \phi_{\mu}(k)| = \sum_\mu |\phi_{\mu}(k)\rangle S^{-1}_{\mu\nu}(k) \langle \phi_{\nu}(k)|$, \hspace{1cm} (2)

where

$$S_{\mu\nu}(k) = \langle \phi_{\mu}(k)| \phi_{\nu}(k) \rangle$$ \hspace{1cm} (3)

is the overlap matrix of the atomic basis, and the vectors $|\phi^{\mu}(k)\rangle$ are the dual of the atomic basis, that satisfy

$$\langle \phi^{\mu}(k)| \phi^{\nu}(k) \rangle = \langle \phi_{\mu}(k)| \phi_{\nu}(k) \rangle = \delta_{\mu\nu}.$$ \hspace{1cm} (4)

$S$ measures the difference between the plane-wave eigenstates $|\psi_{\alpha}(k)\rangle$ and their projection into the atomic-basis $P(k)|\psi_{\alpha}(k)\rangle$. More precisely, it gives the average of $||(1 - P)|\psi_{\alpha}(k)\rangle||^2$ over the eigenstates considered for the projection. The spilling $S$ varies between 0 and 1. $S = 0$ means that the LCAO projected wave-functions reproduce the PW eigenfunctions exactly. $S = 1$ means that the basis is orthogonal to the Hamiltonian eigenstates.

As mentioned above, the quality of an LCAO basis is evaluated not only for a particular system, but also for a particular set of Hamiltonian eigenstates. An LCAO basis will reproduce with very different accuracy the different eigenstates of a Hamiltonian. The choice of eigenstates relevant to the definition of $S$ depends on the particular application. For ground-state properties of the system (total energy, geometry, electronic density, chemical analysis) the occupied eigenstates are the ones to be considered. For quasiparticle excitations or optical properties, some of the lowest empty states should be also included in the projection. As shown later, the latter case typically requires a larger atomic basis.

In addition to the analysis and possible selection of atomic basis sets, the methodology presented in this work allows for their systematic optimization in a straightforward way. Given a type of atomic functions (say Slater-type orbitals, Gaussian-type orbitals) that depend on certain parameters (say exponents) the problem of optimizing the basis becomes minimizing $S$ as a function of those parameters. Note that the minimization requires evaluations of $S$ for different values of the parameters, but for a single first-principles calculation. Taking into account that the evaluation of $S$ represents a minimal computational effort compared with the actual PW calculation, it is obvious that this optimization procedure is much more convenient than the direct trial-and-error procedures using self-consistent LCAO codes.

Using this procedure we have performed a systematic study comparing different kinds of atomic orbitals in different solids. This will be presented in detail elsewhere. In that analysis it is found that for many properties (spilling, charge density and populations, energy bands) the type of atomic orbitals that gives better results is the following: take the eigenfunctions of the free atoms using the same basic approximations as for the solid (LDA, same pseudopotential) and scale them down by scale factors $\lambda_i$ (one scale factor per different atomic orbital), that is, $\phi_i(r) = N_i(\lambda_i)\phi_i^{atom}(\lambda_i r)$, being $N_i(\lambda)$ the normalization factor. The optimum scale factors are determined by minimization of $S$. Typically the orbitals compress by a small amount except for the orbitals which are empty in the atomic calculation that compress substantially. These optimized orbitals are the ones used in the following, except stated otherwise.

A further utility of the projection technique is its suitability for obtaining and analyzing LCAO Hamiltonians (tight-binding parameters) and their associated energy bands. The matrix elements of the projected Hamiltonian

$$H_{\mu\nu}^{LCAO}(k) = \langle \phi_{\mu}(k)|H^{PW}|\phi_{\nu}(k)\rangle$$ \hspace{1cm} (5)

can be obtained using fast Fourier transform algorithms and other techniques of the PW method:

$$H_{\mu\nu}^{LCAO}(k) = \sum_{|k+G| < E_{max}} \frac{\langle \phi_{\mu}(k) | k + G \rangle \langle k + G | H^{PW} | \phi_{\nu}(k) \rangle}{|k + G|}$$ \hspace{1cm} (6)

where $G$ are reciprocal lattice vectors and $E_{max}$ is an energy cut-off independent of the one used in the PW calculation, that must be large enough to guarantee a reliable representation of the atomic basis. It has to be
stressed that the proposed procedure obtains the Hamiltonian matrix elements from first-principles, no free parameters being fitted.

The LCAO Hamiltonian matrix is obtained directly in Bloch space. By construction, it includes the information of the matrix elements between localized functions up to infinite neighbors. This is a very interesting feature of our method for the characterization of a basis in terms of its associated band structure: it conveniently separates the effect of the incompleteness of the basis from the effect of neglecting matrix elements beyond some scope of neighbors. These two sources of error are usually mixed together in the traditional ways of choosing atomic orbitals from their LCAO bands. With our procedure each approximation can be analyzed separately.

To obtain the real-space Hamiltonian matrix elements (tight-binding parameters) from the reciprocal-space Hamiltonian, we perform an inverse Bloch transformation

$$H_{\mu\nu}^{LCAO}(R_{\mu\nu}) = \sum_k H_{\mu\nu}^{LCAO}(k) e^{i \mathbf{k} \cdot (R_{\mu} - R_{\nu})}$$

(7)

where normalization factors which depend on the overlaps are omitted for clarity. The sum has to be extended to a sufficient number of $k$ points, taking into account that the number of points depends on the real space range of the interactions. For silicon and the STO-4G basis used below, interactions are important up to third nearest neighbours and a few tens of $k$ points have proven to be enough.

In Figure 1 (a) and (b) we present the energy bands of silicon for an $sp$ minimal basis and for an $spd$ basis, respectively, with interactions up to infinite neighbors, as obtained from the projection. They are compared with the PW energy bands, that were calculated with a well converged plane-wave basis set. The atomic basis was generated and optimized as explained above, the $d$ orbital being obtained from an excited configuration of the silicon atom. The spilling of charge (considering the sum over occupied states in Eq. 1) is $S = 0.0076$ and $S = 0.0007$ for the $sp$ and $spd$ basis, respectively. The figure shows that the $sp$ basis reproduces the valence band much better than the lowest conduction bands, giving a rather poor description of the band gap. The inclusion of the $d$ orbitals substantially improves both the valence band and the band gap, especially the latter.

The atomic orbitals used above are relatively extended. For some purposes a reduction of their extension is desirable. Figure 2 shows the effects of a contraction of the basis. The energy of the X point rises, showing a tendency to establish a direct band gap, in addition to the expected narrowing of the bands and the overall increase of the gap. The shape and the ordering of the conduction bands is very sensitive to the contraction of the basis. See for example the change in ordering of the $s$ and $p$ conduction states at $\Gamma$ with the change in scale factor. The charge spillings are $S = 0.0076$ and $S = 0.0292$ for the optimum and the contracted basis, respectively.

Even though the energy bands become worse with an overlocalization of the atomic orbitals, this can still be interesting if matrix elements for neighbors beyond a range are wanted to be negligible. The effect of this kind of approximation is shown in Figure 3, where the energy bands for silicon are presented for an STO-4G $sp$ minimal basis\textsuperscript{44} with interactions up to first (a), second (b), and third (c) nearest neighbors. They result from the diagonalization of the LCAO Hamiltonian matrix obtained in Eq. 5, and they are compared with the result of infinite neighbors. We have observed that the atomic basis obtained from the scaled eigenfunctions of the atom usually require a longer range of interactions. The use of STO-4G orbitals reduces the range of non-negligible interactions. However, the quality of the bands (infinite neighbors) for the STO basis (dotted lines in Fig. 3) is worse than for the other basis, showed with solid lines in Fig. 1 (a), as compared with the plane-wave results, shown as dotted lines in Fig. 1. Notice that the optimized basis used for Figure 1 (a) correctly gives an indirect band gap, which is not usually obtained with standard minimal $sp$ basis sets like the one used in Fig. 3. The charge spilling of the STO-4G basis is $S = 0.0513$, considerably larger than for the basis used in Fig. 1 (a) ($S = 0.0076$). In LCAO calculations the extension of the atomic orbitals has to be chosen compromising between the quality required for the band-structure and valence properties, and the possibility of neglecting matrix elements beyond a range. The choice of basis depends on the particular application.

Finally, we show the utility of the projection technique for the analysis of the results of PW calculations by means of LCAO population analysis. We use the one proposed by Mulliken.\textsuperscript{45} The analysis is performed on the occupied eigenstates projected into the subspace of the basis. It has to be done with care since the projected eigenstates $|\chi_\alpha(k)\rangle = P(k)|\psi_\alpha(k)\rangle$ are not orthonormal (the deviation from orthonormality is related with the charge spilled in the projection\textsuperscript{45}). Proper consideration of their associated overlap $R_{\alpha\beta}(k) = \langle \chi_\alpha(k)|\chi_\beta(k)\rangle$ is necessary to ensure charge conservation in the population analyses. This is accomplished by defining the density operator as

$$\hat{\rho} = \sum_{k} \sum_{\alpha} \langle \chi_\alpha(k)|\chi_\alpha(k)\rangle,$$

(8)

where $|\chi_\alpha(k)\rangle = \sum_\beta R_{\alpha\beta}^{-1}(k)|\chi_\beta(k)\rangle$ represent the vectors of the dual set of the projected eigenstates. The LCAO density matrix is then written in terms of the dual LCAO basis:

$$P_{\mu\nu} = \langle \phi^{\mu}|\hat{\rho}|\phi^{\nu}\rangle,$$

(9)

the charge associated to an orbital $\mu$ then being

$$Q_\mu = \sum_{\nu} P_{\mu\nu} S_{\nu\mu}.$$

(10)

Results of this procedure are shown in Table I, where charge transfers are calculated for different heteropolar
zincblende materials. They are compared with results of self-consistent LCAO calculations showing a remarkable agreement. The basis functions used for these population analysis are the scaled atomic orbitals discussed above, which showed to be best suited for the purpose.

In summary, it has been shown how the simple projection of the eigenstates obtained from PW calculations into the space spanned by an LCAO basis can be useful for multiple purposes: (i) to evaluate and optimize LCAO basis sets, (ii) to analyze LCAO band structures, (iii) to obtain tight-binding parameters, and (iv) to perform population analysis. The procedures are straightforward and more systematic than the previous methods. The main idea of this paper could also be used for the improvement of first-principles algorithms. This possibility is presently being explored.

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FIG. 1. Electronic band structure of silicon calculated projecting the plane-wave LDA Hamiltonian into an sp atomic basis (a), and into an spd atomic basis (b), both shown in solid lines. Dotted lines show the plane-wave LDA band structure. The basis functions are obtained as discussed in the text.

FIG. 2. Effect of different contractions of an sp atomic basis in the silicon band structure. Solid lines are for optimum scale factors and dotted lines for a further contraction of the basis functions of a 1.2 factor. The basis functions are obtained as discussed in the text.

FIG. 3. Band structure of silicon as a function of the range of non-neglected interactions: interactions up to first (a), second (b), and third (c) nearest neighbors. In dotted lines the result for infinite neighbors is shown as reference (in (c) they are hardly distinguishable from the solid lines). The atomic basis functions are standard STO-4G taken from Ref. 10.

TABLE I. Calculated charge transfer for some zincblende semiconductors. $Q_C$ and $Q_A$ stand for the valence charge on the cation and the anion, respectively, $\delta Q$ for the charge transfer with respect to neutral atoms, and $S$ for the spilling. Numbers in parenthesis were obtained from Hartree-Fock LCAO calculations, except for GaAs, for which LDA LCAO was used.

| Basis | S | $Q_C$ | $Q_A$ | $\delta Q$ |
|-------|---|-------|-------|-----------|
| BN    | $s, p$ | 0.0022 | 2.19 (2.14) | 5.81 (5.86) | 0.81 (0.86) |
| BP    | $s, p$ | 0.0038 | 3.51 (3.34) | 4.49 (4.66) | 0.51 (0.34) |
| AlP   | $s, p$ | 0.0035 | 2.15 (2.20) | 5.85 (5.80) | 0.85 (0.80) |
| SiC   | $s, p$ | 0.0071 | 2.30 (2.19) | 5.70 (5.81) | 1.70 (1.81) |
| GaAs  | $s, p, d$ | 0.0041 | 2.58 | 5.42 | 0.42 |
|       | $s, p, d$ | 0.0010 | 2.78 (2.88) | 5.22 (5.12) | 0.22 (0.12) |
