

## Direct space symmetry adaptation of crystal orbitals

JEAN-LOUIS CALAIS

Quantum Chemistry Group, University of Uppsala, Box 518, S-751 20-uppsala, Sweden

**Abstract.** Symmetry adaptation of crystal orbitals normally means that one constructs functions transforming according to the irreducible representations of a space group. In the present paper we discuss certain drawbacks with such a procedure and point out the need for a method which avoids the detour into reciprocal space.

**Keywords.** Symmetry adaptation; crystal orbital; direct space; generalized Wannier function; localization.

### 1. Introduction

The connection between the concepts of localization, orthonormalization and symmetry adaptation of crystal orbitals has been analyzed in two recent papers (Calais 1985a, b). The three properties associated with these concepts are all desirable for orbitals to be used in calculations of the electronic structure of solids. Symmetry adaptation of a set of functions is a well defined procedure described in most text books on group theory. It can be carried out in different ways, though, and this is an aspect which will be discussed in the present paper. Symmetry adapted orbitals associated with different symmetries are by definition orthogonal. If they belong to the same symmetry species one must however invoke some type of orthogonalization procedure. Both symmetry adaptation and orthogonalization involve mixing of functions, and inasfar as these functions are localized atomic orbitals both procedures may therefore lead to an increased delocalization. The relation between localization and orthogonalization is however rather subtle and it seems a little premature to claim that the two are mutually exclusive (Levy and Berthier 1977).

The symmetry adaptation traditionally used for crystal orbitals is based on the concept of the group of the wave vector (Cornwell 1969; Bradley and Cracknell 1972). This term is used both for symmorphic groups, where it is a subgroup of the point group associated with the space group, and for non-symmorphic groups, where it contains the translation group as a subgroup, and thus forms a subgroup of the space group. Bradley and Cracknell (1972) distinguish these two groups by the terms 'little co-group of the wave vector' (a subgroup of the point group) and 'little group of the wave vector' (a subgroup of the space group).

For a symmorphic group the irreducible representations are of the form

$$D(\{R|\mathbf{m}\}) = e^{i\mathbf{k}\cdot\mathbf{m}}\Gamma(R), \quad (1)$$

where  $\Gamma(R)$  is an irreducible representation of the little co-group of  $\mathbf{k}$ . We use the conventional notation for space group elements with  $R$  denoting the point group

---

Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

operation and  $\mathbf{m}$  a translation (which is always primitive for a symmorphic group). Its operation on a vector  $\mathbf{r}$  is given by

$$\{R|\mathbf{m}\}\mathbf{r} = R\mathbf{r} + \mathbf{m}. \quad (2)$$

For non-symmorphic groups the construction of the irreducible representations is a little more complicated, but there also we need the irreducible representations of the group of the wave vector—with the meaning ‘little group of  $\mathbf{k}$ ’. Of all these irreducible representations only those satisfying

$$\Gamma^{(p)}(\{1|\mathbf{m}\}) = e^{-i\mathbf{k}\cdot\mathbf{m}} \Gamma^{(p)}(\{1|0\}), \quad (3)$$

are however useful in the sense that the basis functions associated to them can be used to form basis functions for the space group.

This traditional approach has dominated the scene since these concepts and procedures were introduced in the thirties. It is the natural approach if one works in reciprocal space and is primarily interested in the extended eigenfunctions of the one electron Hamiltonian. A ‘complementary’ perspective based on direct space concepts has always existed, and this approach has been gaining ground in recent years (Anon 1980), both as an alternative way of handling the ordinary band theory problem (Calais 1985b; von Boehm and Calais 1979), and as the more natural way of treating problems where the translation symmetry is no longer present.

This direct space perspective requires a different way of handling the symmetry adaptation. Very important work has been done in that area by, among others, des Cloizeaux (1963, 1964) and Zak (1980; 1981a, b). Probably because relatively few scientists seem to have been interested in this type of problem much remains to be done, however. In the present paper we review some of the drawbacks of the ‘traditional approach’ (§2) and some aspects of the results obtained so far ‘in direct space’ (§3). In the last section we discuss several possibilities of reaching the final goal. In particular we try to point out what ingredients of the presently known procedures are likely to be valuable.

The paper is thus of an exploratory nature which should not be surprising since the problems encountered are not yet solved in a way leading to simple efficient procedures for creating a set of *completely orthonormal, symmetry adapted crystal orbitals*. We hope that the discussions in this paper will stimulate further work towards that goal.

## 2. Problems in the traditional formulation

A basis of atomic like orbitals localized in ordinary space is definitely preferable for a number of problems in solid state physics (Anon 1980). It is desirable to take maximum advantage of the symmetry of the crystal, and the overlap problem must be handled in one way or another. At the same time one must try to avoid that symmetry adaptation and orthogonalization destroy the localization of the original functions completely. It is still an open question whether these requirements are compatible or not.

One possible procedure is described earlier (Calais 1985a). Starting out from a set of atomic orbitals (AO)  $\phi_\lambda(\mathbf{m}, \mathbf{r})$ , localized (or rather labelled) by the unit cell index  $\mathbf{m}$  and the compound subscript  $\lambda$  standing for position in the unit cell and type of orbital, one first finds the irreducible components  $\phi_{\lambda_s}(\mathbf{r})$  with respect to the little co-group  $\bar{G}^{\mathbf{k}}$  of a wave vector  $\mathbf{k}$ . This means that the functions  $\phi_{\lambda_s}(\bar{\mathbf{r}})$  transform according to the  $s$ th row

of the irreducible representation (IR)  $\Gamma_p$  of  $\bar{G}^{\mathbf{k}}$ . Then one forms Bloch sums of these functions, which are thus symmetry adapted both to  $\bar{G}^{\mathbf{k}}$  and to the translation group. The resulting Bloch sums are orthogonal with respect to the three symmetry labels  $\mathbf{k}$ ,  $p$ ,  $s$  but *not* with respect to  $\lambda$ . In order to get a basis for an IR of the full space group one must also operate on the Bloch sums with the representatives of the star of  $\mathbf{k}$ . For each set of symmetry labels we now have a set of functions labelled by  $\lambda$  with a non unit overlap matrix. In Calais (1985a) it is proposed to make a symmetric orthonormalization of these functions in order to get a set of completely orthonormal, symmetry adapted functions.

The functions constructed according to this prescription are Bloch functions, which implies that they are extended throughout the crystal. Given a set of Bloch functions  $\psi(\mathbf{k}, \mathbf{r})$  with  $\mathbf{k}$  running through the whole first Brillouin zone (BZ) one can construct an associated set of Wannier functions by means of the unitary transformation,

$$W(\mathbf{m}, \mathbf{r}) = [1/(N)^{1/2}] \sum_{\mathbf{k}}^{\text{BZ}} \psi(\mathbf{k}, \mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{m}} \quad (4)$$

As proposed by von Boehm and Calais (1984) this can be done also with the completely orthonormal, symmetry adapted functions described earlier. The resulting functions will at least be *labelled* by the unit cell index  $\mathbf{m}$ . Whether they still possess any local properties is an open question.

The procedure just described means that we start out in ordinary space, make a detour in reciprocal space, and then return to ordinary space. The reason for this 'detour' is the fact that the IR of a space group are characterized by—among other symbols—the wave vectors  $\mathbf{k}$  in BZ. Another way to describe this detour is to say that out of localized functions (in ordinary space) we first form extended ones which are finally combined to functions which are again somehow localized.

The most cumbersome 'technical' problem in this procedure is probably the final orthonormalization. First one has to calculate—for a fairly large number of wave vectors and for all symmetry species of the corresponding little co-groups—the overlap matrices. Each such matrix has to be diagonalized so that one can construct the inverse half power of it, which is necessary for the symmetric orthonormalization. There are other methods for constructing  $\Delta^{-1/2}$  but in general we can hardly expect a power series expansion to be sufficient. Thus the proposed procedure suffers primarily from a drawback 'on principle'. There are also certain technical problems, which, although perfectly tractable, make the method less attractive. At least intuitively it would seem possible to achieve the same or an equivalent goal in a more direct way.

### 3. Direct space concepts

In a paper of far reaching importance des Cloizeaux (1963) has shown that symmetry adapted *local* orbitals can be used for analysis of the eigenfunctions of a one electron crystal Hamiltonian. A central concept in his method is the group  $G_M$  containing all those elements of the space group  $G$  which leave the point  $M$  invariant.  $G_M$  is thus a subgroup of the full space group. The Wannier functions which are associated with  $M$  form a basis for an IR of  $G_M$ . Since  $G_M$  is a subgroup of  $G$ , one can subduce representations of  $G_M$  (in general reducible) from the IR of  $G$ .

Building on the results obtained by des Cloizeaux, Zak (1980, 1981a,b) has

developed a number of very interesting concepts which deserve to be used much more widely than has been the case so far. In particular he has stressed the need for a representation which describes the symmetry of a band *as a whole*. A band in this connection is always an *isolated* band. In general it contains several branches which touch at some points or along some lines in BZ. In a given band there is a fixed number  $f$  of states associated with each wave vector  $\mathbf{k}$ . All the Bloch functions associated with such an  $f$ -fold band span its *band space*. It is then possible to construct functions in that space which transform according to what Zak calls a *band representation* of the space group.

The band representation is a somewhat elusive concept which needs to be analyzed further. It is related to the representations of the 'local' groups  $G_M$  of des Cloizeaux.  $G_M$  being a subgroup of the full space group  $G$  one can make a coset decomposition of  $G$  with respect to  $G_M$ . If the band representations of  $G_M$  are known one can induce those of  $G$ . The band representation is closely connected with the symmetry of the Wannier functions. Direct and reciprocal space are inseparable precisely for symmetry reasons. Concepts associated with the wave vector are central to the construction of the IR of the space group. Still the concepts just sketched—the local group  $G_M$ , which forms as it were a counterpart in direct space to the group of the wave vector, and the band representations—would seem to provide raw material for a more 'direct' symmetry adaptation in ordinary space.

#### 4. Discussion

des Cloizeaux (1963) has outlined a procedure for constructing what he calls generalized Wannier functions. He chooses a point  $M_0$  and introduces a set of orbitals centred at  $M_0$  which form a basis for an IR of  $G_{M_0}$ . The space group elements generate the points  $M$  which form the lattice of  $M_0$ . From the orbitals centred at  $M_0$  he constructs the corresponding orbitals centred at  $M$ . He also shows that all these orbitals (a set at each lattice point) are completely orthonormal. Their localization is a much more difficult problem which des Cloizeaux has treated in subsequent papers (des Cloizeaux 1964).

The starting point for this procedure is a set of orthonormal functions which form a basis for an IR of  $G$  and for those IR of  $G_{M_0}$  which are subduced from it. The 'traditional' method (Calais 1985a) provides bases for the IR of  $G$ , and out of those one can construct the required starting functions. This is in fact the method developed in (von Boehm and Calais 1984). As indicated earlier it has certain drawbacks.

The combination of symmetric and successive orthonormalization proposed by Löwdin (1956) avoids these drawbacks, since it works exclusively in ordinary space. The price to pay gets rather high, though. Given a lattice with a set of  $p$  orbitals in each unit cell, one first constructs symmetrically orthonormalized orbitals for each *type* of orbital. Efficient methods for doing that exist (Löwdin *et al* 1960; Calais and Appel 1964). The result is a set of  $p$  functions 'in' each unit cell such that functions of the same type in different unit cells are orthogonal, whereas functions of different type both in the same and in different unit cells are not. Expressed in another way we have  $p$  *sets* of orbitals such that within each set the orbitals are orthonormal. Löwdin (1956) proposed to make a successive orthonormalization of the *sets* in cases when that is motivated 'physically'. One can certainly apply any type of orthonormalization to the *sets* in order

to achieve the goal: completely orthonormal orbitals. If the number  $p$  is small this procedure is certainly feasible and it has been used in practice. It does however involve a fairly large number of functions of all the overlap matrices and it gets quite cumbersome when  $p$  increases. It can certainly be combined with symmetry adaptation but then the successive orthonormalization will require special treatment.

Thus it is easy to 'create local symmetry' or to form functions which like the Wannier functions are orthonormal if centred in different unit cells. What is difficult is to combine both procedures.

A possible path might involve a combination of des Cloizeaux and Löwdin's methods. The former can prove a number of important results because he starts out with rather far reaching assumptions. The latter's procedures can be applied directly to a given material, but since they easily get rather cumbersome it would be very useful if they could be simplified by means of some group theoretical results.

The term 'type of orbital' which has been used here refers both to position in the unit cell and to the particular function centred there. Any position in a unit cell can serve as the starting point for a lattice and a combination of local symmetry adaptation and des Cloizeaux' methods would seem promising. On the other hand we must also be able to handle the case when a set of positions in a unit cell are suitable centres for orbitals and it is not immediately clear how to apply his procedures in such a case.

### Acknowledgement

This work was supported by the Swedish Natural Sciences Research Council.

### References

- Anon, Bullett D W, Haydock R, Heine V and Kelly M J 1980 *Solid State Phys.* **35**  
Bradley C J and Cracknell A P 1972 *The mathematical theory of symmetry in solids* (Oxford: Clarendon Press)  
Calais J-L 1985a *Int. J. Quantum Chem. Symp.* **19**  
Calais J-L 1985b *Phys. Scripta* **31**  
Calais J-L and Appel K 1964 *J. Math. Phys.* **5** 1001  
Cornwell J F 1969 *Group theory and electronic energy bands in solids* (Amsterdam: North-Holland)  
des Cloizeaux J 1963 *Phys. Rev.* **129** 554  
des Cloizeaux J 1964 *Phys. Rev.* **135** A685, A698  
Lévy B and Berthier G 1977 *Int. J. Quantum Chem.* **12** 579  
Löwdin P-O 1956 *Adv. Phys.* **5** 1  
Löwdin P-O, Pauncz R and de Heer J 1960 *J. Math. Phys.* **1** 461  
von Boehm J and Calais J-L 1979 *J. Phys.* **C12** 3661  
von Boehm J and Calais J-L 1984 *J. Phys.* **C17** 249  
Zak J 1980 *Phys. Rev. Lett.* **45** 1025  
Zak J 1981a *Phys. Rev.* **B23** 1704, 2824  
Zak J 1981b *Phys. Rev. Lett.* **47** 145, 450