

On the Validity of the Cluster Method for Crystals

PAULO S. GUIMARÃES

Instituto de Pesquisas Espaciais, São José dos Campos, 12.200, SP, Brasil

and

LUIZ G. FERREIRA

Instituto de Física, Universidade de São Paulo, Caixa Postal 20.516, São Paulo, 01000, SP, Brasil

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Abstract A formal mathematical background is developed in such a way that it determines the necessary conditions that a cluster must satisfy to reproduce accurately the main features of the band structure of an infinite crystal. It has been shown that if such conditions are satisfied the cluster energy band structure is a true image of the crystal one. It has been also shown that the larger the band gaps in the crystal, the smaller is the cluster needed to represent its band structure.

1. INTRODUCTION

Small clusters of atoms have been used to reproduce the electronic band structure of infinite crystals. As it has been made clear by Kadura and Kunne¹, in some instances, the reduction of an infinite crystal to a few atoms does not preserve the main features of the band structure. For instance, in the case of metals, these authors showed that clusters with more than 100 atoms are needed to reproduce the crystal band structure. Thus, we first address ourselves to the question of the validity of a cluster calculation.

When a cluster band structure calculation is performed, one expects that the energy bands of the cluster are a good image of the bands of the infinite crystal, in other words, one expects that the cluster preserves those features of the crystal bands that have a strong local character and result from short range interactions. For instance, we cannot expect that a cluster calculation gives the location of the band maxima and minima in the Brillouin zone, but we can expect it to give the correct charge density and a passable energy density of states. In most cluster calculations we have seen, one avoids answering the important questions of what are the infinite crystal features preserved by the cluster and how is one to proceed to preserve them. It is frequent,

for instance, that a cluster calculation gives an energy spectrum which is a mixture of bulk and surface states². In our mind, an exception is the work by Brescansin and Ferreira³. In their self-consistent calculation of NaCl, in spite of the Schrödinger equation being solved in the cluster, they try to preserve the crystal features by solving the Poisson equation in the infinite crystal. Without repeating their intuitive arguments here, we intend to show that the Brescansin and Ferreira procedure has a firm theoretical basis, and, in this process, we make clear what are the preserved infinite crystal features. For instance, we conclude that metals cannot be calculated but with very large clusters, and that, for insulators, the cluster bandwidths are narrower than those of the crystal and the cluster gaps are larger.

As long as it has been well tested, a cluster calculation is a fast method of electronic band structure determination and, when it is reliable, a cluster calculation has many advantages. For instance, the calculation of deep defect levels is simple if one uses a cluster⁴, but it becomes very difficult when the whole infinite crystal is used. Beyond this fact, a cluster calculation becomes specially simple and fast within the framework of the multiple-scattering method⁵. This is a precise method as long as the effects of the muffin-tin potential are small, in other words, as long as the cluster is dense. Thus, a muffin-tin cluster calculation must test for the importance of the potential errors and for the importance of the cluster size effects.

2. A JUSTIFICATION OF THE CLUSTER MODEL OF A CRYSTAL

A self-consistent field calculation requires the simultaneous solution of two differential equations: the Schrödinger equation, solved for each electron, and the Poisson equation. In the Brescansin and Ferreira procedure, the Poisson equation is solved in the infinite crystal, using the charge densities of the inner atoms of the cluster as representative charge densities in the crystal. In the multiple-scattering method these charge densities are in the muffin-tin format and the solution of the Poisson equation in the infinite crystal presents no special difficulty. The muffin-tin potential, thus obtained, is used in the Schrödinger equation for the cluster, but one has to surround the cluster atoms by a potential barrier in such a way as to confine the elec-

trons in the region where the potential is well defined. The advantages of this procedure have been stressed by Bressanin and Ferreira and will not be repeated here. While they present an intuitive justification of their procedure, we are giving a formal and exact mathematical justification, which has the advantage of exhibiting clearly the limitations of the cluster method.

Cluster calculations following very different procedures have been presented in the literature. Most of them are very difficult to justify and as far as we know, this is the first time a justification is presented which goes beyond the purely intuitive arguments.

We begin our discussion of the Bressanin and Ferreira muffin-tin cluster method by studying the following one-electron Hamiltonian

$$\hat{H} = \hat{H}_0 + A \sum_n \sum_{|\vec{k}| > R_0} \hat{P}_{n, \vec{k}} \quad (1)$$

where \hat{H}_0 is the Hamiltonian for an electron in the infinite crystal and A is a large and positive number. The sum in n is a sum over the bands of the infinite crystal, while the sum in \vec{k} is a sum over the lattice vectors whose moduli are larger than the radius R_0 . Finally, $\hat{P}_{n, \vec{k}}$ is a projection operator that projects into the state of the Wannierfunction of band n centered at site \vec{k} . In the coordinate representation, one writes

$$\hat{P}_{n, \vec{k}} \psi(\vec{r}) = \int d^3 \vec{r}' a_n(\vec{r} - \vec{k}) a_n(\vec{r}' - \vec{k})^* \psi(\vec{r}') \quad (2)$$

where $a_n(\vec{r} - \vec{k})$ are the Wannier functions.

The definition of a Wannier function is not unique because it depends on the phases attributed to the Bloch functions in the whole Brillouin zone. In what follows, it will be convenient to define the Wannier functions so that they have minimal widths W_n defined as follows

$$W_n^2 = \int d^3 \vec{r} a_n(\vec{r})^* r^2 a_n(\vec{r}) \quad (3)$$

The problem of defining these minimal Wannier functions has been solved by Ferreira and Parada⁶, and one can construct the projection opera-

tors $P_{n, \vec{\ell}}$ in Eq. (1) according to their prescriptions. In the case of overlapping bands we can do even better. Consider, for instance, the case of the Cl 3p bands in NaCl. In this case, there are three bands overlapping in energy and that are degenerated at symmetry points in the Brillouin zone. Instead of defining a Wannier function for each band, we could combine the Bloch functions of the three bands as

$$a_n(\vec{r} - \vec{\ell}) = \frac{1}{\Omega^{1/2}} \int d^3\vec{k} e^{-i\vec{k} \cdot \vec{\ell}} \sum_m U_{nm}(\vec{k}) b_m(\vec{k}, \vec{r}) \quad (4)$$

where Ω is the volume of the Brillouin zone, $b_m(\vec{k}, \vec{r})$ are the Bloch functions corresponding to such bands and U_{nm} is a k -dependent unitary matrix. The new Wannier functions obey the required orthonormality relations

$$\int d^3\vec{r} a_n(\vec{r} - \vec{\ell})^* a_{n'}(\vec{r} - \vec{\ell}') = \delta_{n, n'} \delta_{\vec{\ell}, \vec{\ell}'} \quad (5)$$

and the unitary matrix $U_{nm}(\vec{k})$ might be chosen so that the Wannier functions of Eq. (4) had minimal widths. In the case of the three Cl 3p bands, since the Bloch functions are primarily made out of atomic Cl 3p functions, the minimal Wannier functions defined in Eq. (4) would have widths at most equal to the width of the atomic functions. Thus, in what follows we shall keep in mind that one is able to construct Wannier functions with widths of the order of an atomic radius. These Wannier functions are those used in the definition of the projection operators of Eq. (1).

The effect of the second term in Eq. (1) is simple to understand: this term raises the energy of the electron if it ventures outside the sphere of radius R_0 . Now, suppose we find the eigenfunctions and eigenvalues of Eq. (1). Since the Hamiltonian commutes with the projection operator of the bands

$$\hat{H} \hat{P}_n = \hat{P}_n \hat{H}$$

where

$$\hat{P}_n = \sum_{\vec{\ell}} \hat{P}_{n, \vec{\ell}}$$

each eigenstate of \hat{H} is a combination of the Bloch states of a *single band*. Working in the Wannier representation, the secular matrix of the Hamiltonian \hat{H} of Eq. (1) assumes the following form

$$\hat{H} = \begin{vmatrix} \langle \vec{x} | \hat{H}_0 | \vec{x}' \rangle & \langle \vec{x} | \hat{H}_0 | \vec{x}''' \rangle \\ \hline \langle \vec{x}'' | \hat{H}_0 | \vec{x}' \rangle & \langle \vec{x}'' | \hat{H}_0 | \vec{x}''' \rangle \\ & +A \delta_{\vec{x}'', \vec{x}'''} \end{vmatrix} \quad (6)$$

This matrix breaks into the following four submatrices: the upper-left diagonal submatrix refers to the internal Wannier function states, namely

$$|\vec{x}\rangle, |\vec{x}'\rangle \in R_0, \quad ,$$

the lower-right diagonal submatrix refers to the external Wannier functions, or

$$|\vec{x}''\rangle, |\vec{x}'''\rangle \in R_0, \quad ,$$

while the off-diagonal matrices mix the external with the internal Wannier function states. If A is sufficiently large (later on it will become clear how large it must be) the determinantal equation of the matrix of Eq. (6) can be solved by perturbation theory. Setting

$$\hat{H} = \hat{H}^{(0)} + \hat{V}$$

where

$$\hat{H}^{(0)} = \begin{vmatrix} \langle \vec{x} | \hat{H}_0 | \vec{x}' \rangle & 0 \\ \hline 0 & \langle \vec{x}'' | H_0 | \vec{x}''' \rangle \\ & +A \delta_{\vec{x}'', \vec{x}'''} \end{vmatrix}$$

we obtain

$$\hat{V} = \begin{vmatrix} 0 & | & \langle \vec{x} | \hat{H}_0 | \vec{x}' \rangle \\ \hline \langle \vec{x}'' | \hat{H}_0 | \vec{x}' \rangle & | & 0 \end{vmatrix}$$

The eigenvalues of $\hat{H}^{(0)}$ (not to be confused with \hat{H}_0) are the discrete eigenvalues of the upper-left submatrix and the continuous eigenvalues of the infinite lower-right submatrix.

In figure 1 we show the spectra of the eigenvalues of \hat{H}_0 and $\hat{H}^{(0)}$. Each band of \hat{H}_0 is broken into a higher continuous band, displaced

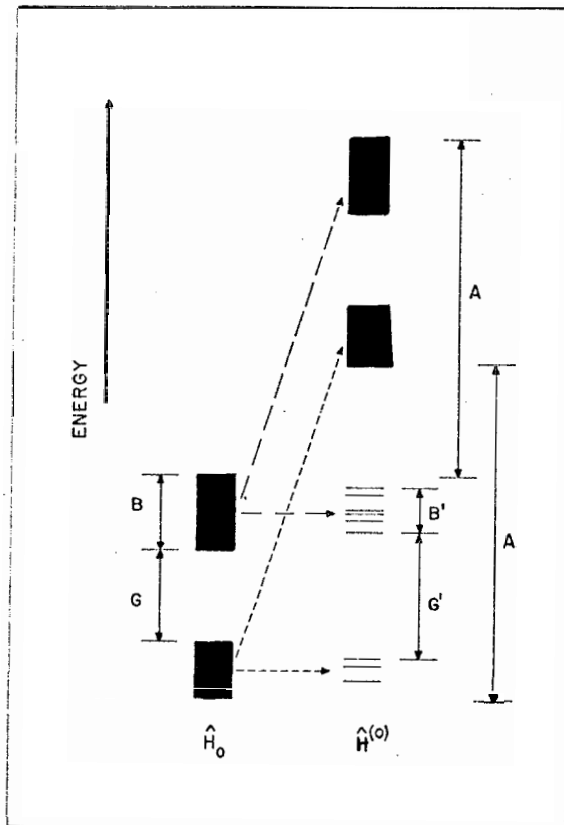


Fig. 1 - Energy eigenvalue spectrum of the cluster Hamiltonian as compared to the crystal Hamiltonian spectrum.

from the original band by A , and a set of discrete states with energies between the highest and lowest energies of the original bands. The effect of the perturbation of \hat{V} is negligible if A is large. Indeed, from second-order perturbation expansion, one knows that \hat{V} displaces the discrete eigenvalues of $\hat{H}^{(0)}$ by

$$\frac{|\langle \vec{x} | \hat{H}_0 | \vec{x}' \rangle|^2}{A}$$

Now, the off-diagonal matrix elements of \hat{H}_0 have the order of magnitude of the bandwidth E . Thus, if A is much larger than the bandwidth, the perturbation of \hat{V} can be neglected and the eigenvalues of \hat{H} will coincide with those of $\hat{H}^{(0)}$.

In any cluster calculation we are interested in the discrete spectra made out of the continuous states of the band. According to the preceding argument, if the cluster calculation is made with the Hamiltonian of Eq. (1), and as long as A is much larger than the bandwidth, the discrete states are exact combinations of the internal Wannier functions of a single band, that is

$$\psi^{(0)}(\vec{x}) = \sum_{|\vec{x}'| < R_0} \alpha(\vec{x}') a_n(\vec{x} - \vec{x}') \quad (7)$$

The Wannier functions themselves are combinations of the Bloch eigenfunctions. Thus, the highest discrete state corresponding to a band has a lower energy than the top of the band, and the lowest discrete state is higher than the band minimum. Thus, it can be concluded that, in Figure 1 for instance, the bandwidth B' determined by the cluster is smaller than the true bandwidth B , while the gap separating consecutive bands, G' , is larger than G . On the other hand, if the cluster size is increased, by including more atoms in the calculation, the bandwidth can only increase and the gaps decrease.

What distinguishes the Bressanin and Ferreira self-consistent cluster calculation from other cluster procedures is their treatment of

the Poisson equation. In the usual molecular cluster calculations the discrete states of the cluster are populated with electrons and the resulting charge density is used to solve the Poisson equation for the cluster. On the other hand, in the Bescansin and Ferreira procedure the discrete states are populated, the charge density of the inner atoms is repeated in an infinite net, and such a periodic charge density is used to solve the Poisson equation in this *infinite* crystal.

The Coulomb interaction being of long range, the potential generated in molecular cluster procedures may have strong surface contributions and may be heavily dependent on the size of the cluster. Then the cluster energy spectrum is only a true image of the crystal spectrum if it can be proved that the resulting surface effects are small. This proof is usually absent in the cluster calculations. On the other hand, in the Bescansin and Ferreira procedure, there are no surface effects because the Poisson equation is solved in the infinite crystal, but one must prove that the charge density of the inner atoms of the cluster is truly equal to the charge density of the atoms in the crystal. Thus, we now address ourselves to this point.

Populating *all* discrete cluster states of a band is equivalent to generating an electronic density given by

$$\rho_{\text{cluster}} = \sum_{|\vec{\ell}| < R_0} |a_n(\vec{r} - \vec{\ell})|^2 \quad (8)$$

When compared to the crystal density

$$\rho_{\text{crystal}} = \sum_{\vec{\ell}} |a_n(\vec{r} - \vec{\ell})|^2 \quad (9)$$

Eq. (8) leaves out from the inner atoms the contributions due to the external Wannier functions $a_n(\vec{r} - \vec{\ell})$ with $|\vec{\ell}| > R_0$. If the Wannier functions have small enough widths (Eq. (3)), the contribution left out is very small. As argued before, for the minimal Wannier functions defined in Eq. (4), the width has the order of an atomic radius and thus it is not difficult to make the cluster density of charge coincident with the true crystal density at the inner atoms. Further, as it has been showed by Ferreira and parada⁷, the width of a Wannier function of a band increa-

ses as the energy gaps separating the band from the others decreases. Thus, for a precise charge density at the inner atoms, larger cluster are needed for the smaller gap insulators or semiconductors for the simple reason that the left-out terms in Eq. (8) have longer range.

The preceding paragraph omits a reference to the case of metals because, for their half-filled bands, the electronic density is not given by Eq. (9) and, if we were to populate fractionally the discrete states of the cluster, the electronic density would not be given by Eq. (8). Thus, for a metal, a cluster has no true justifications. As we see it, a metal is a system where the interactions are of very long range and cannot be understood by means of small clusters of atoms.

As a final point, one notices that the Hamiltonian of Eq. (1) is totally impractical. In order to define \hat{H} , one needs to know the Wannier functions, but that is the knowledge we do not have at the beginning of the calculation. In the Brescansin and Ferreira procedure, ones uses instead the following Harniltonian

$$\hat{H}' = \hat{H}_0 + A \Theta(x - R_0). \quad (10)$$

So we must compare the second terms in Eq. (10) and (1).

In the Wannier representation the secular matrix of \hat{H}' is given by

$$\hat{H}' = \begin{array}{c|c} \begin{array}{l} \langle \vec{x} | \hat{H}_0 | \vec{x}' \rangle \\ + A \langle \vec{x} | \Theta(x - R_0) | \vec{x}' \rangle \end{array} & \begin{array}{l} \langle \vec{x} | \hat{H}_0 | \vec{x}'' \rangle \\ + A \langle \vec{x} | \Theta(x - R_0) | \vec{x}'' \rangle \end{array} \\ \hline \begin{array}{l} \langle \vec{x}'' | \hat{H}_0 | \vec{x}' \rangle \\ + A \langle \vec{x}'' | \Theta(x - R_0) | \vec{x}' \rangle \end{array} & \begin{array}{l} \langle \vec{x}'' | \hat{H}_0 | \vec{x}'' \rangle \\ + A \langle \vec{x}'' | \Theta(x - R_0) | \vec{x}'' \rangle \end{array} \end{array} \quad (11)$$

As in the case of Hamiltonian \widehat{H} , one may rewrite Eq. (11) as

$$\widehat{H}' = \widehat{H}^{(0)} + \widehat{V}' \quad (12)$$

where

$$V' = \begin{array}{c|c} A \langle \vec{x} | \Theta(x-R_0) | \vec{x}' \rangle & \begin{array}{l} \langle \vec{x} | \widehat{H}_0 | \vec{x}'' \rangle \\ + A \langle \vec{x} | \Theta(x-R_0) | \vec{x}''' \rangle \end{array} \\ \hline \begin{array}{l} \langle \vec{x}'' | \widehat{H}_0 | \vec{x}' \rangle \\ + A \langle \vec{x}'' | \Theta(x-R_0) | \vec{x}' \rangle \end{array} & \begin{array}{l} A \langle \vec{x}'' | \Theta(x-R_0) | \vec{x}''' \rangle \\ - A \delta_{\vec{x}'', \vec{x}'''} \end{array} \end{array} \quad (13)$$

Then, up to second order perturbation theory, one has that the secular matrix elements for the discrete states of H' are given by:

$$\begin{aligned} (\widehat{H}')_{\vec{x}, \vec{x}'} &= (\widehat{H}^{(0)})_{\vec{x}, \vec{x}'} \\ &+ \frac{1}{A} \sum_{|\vec{x}''| > R_0} \langle \vec{x} | \widehat{H}_0 | \vec{x}'' \rangle \langle \vec{x}'' | \widehat{H}_0 | \vec{x}' \rangle \\ &+ A \langle \vec{x} | \Theta(x-R_0) | \vec{x}' \rangle \\ &+ A \sum_{|\vec{x}''| > R_0} \langle \vec{x} | \Theta(x-R_0) | \vec{x}'' \rangle \langle \vec{x}'' | \Theta(x-R_0) | \vec{x}' \rangle \\ &+ \sum_{|\vec{x}''| > R_0} \{ \langle \vec{x} | \widehat{H}_0 | \vec{x}'' \rangle \langle \vec{x}'' | \Theta(x-R_0) | \vec{x}' \rangle \\ &+ \langle \vec{x} | \Theta(x-R_0) | \vec{x}'' \rangle \langle \vec{x}'' | \widehat{H}_0 | \vec{x}' \rangle \} \end{aligned} \quad (14)$$

The first two terms in Eq. (14) are the same as have been for Hamiltonian \widehat{H} and assure that if A is much larger than the bandwidth, the corresponding perturbation is negligible.

Letting C be the maximum eigenvalue of the matrix

$$\langle \vec{\mathcal{L}} | \Theta(x - R_0) | \vec{\mathcal{L}}' \rangle$$

where both \vec{R} and $\vec{\mathcal{L}}'$ are Wannier functions inside the sphere R_n , the third term becomes negligible if A is chosen so that

$$AC \ll B \quad (15)$$

where B is the bandwidth. For the fourth term we write

$$\text{Max Eigenvalue } \left\{ \sum_{|\vec{\mathcal{L}}'| > R_0} \langle \vec{\mathcal{L}} | \Theta(x - R_0) | \vec{\mathcal{L}}' \rangle \langle \vec{\mathcal{L}}' | \Theta(x - R_0) | \vec{\mathcal{L}} \rangle \right\} \leq$$

$$\leq \text{Max Eigenvalue } \sum_{\text{all } \vec{\mathcal{L}}'} \langle \vec{\mathcal{L}} | \Theta(x - R_0) | \vec{\mathcal{L}}' \rangle \langle \vec{\mathcal{L}}' | \Theta(x - R_0) | \vec{\mathcal{L}} \rangle$$

$$= \text{Max Eigenvalue } \left[\langle \vec{\mathcal{L}} | \Theta(x - R_0) | \vec{\mathcal{L}} \rangle \right] = C$$

Again, this fourth term is negligible when inequality (15) is satisfied.

Finally, the fifth term is of the order of BC and becomes much smaller than B^2/A if inequality (15) is satisfied. Thus, the cluster method of Bressanin and Ferreira is exact if one is able to choose a value of A such that

$$B \ll A \ll B/C \quad (16)$$

where B is the bandwidth and C is the maximum eigenvalue of the matrix

$$\langle \vec{\mathcal{L}} | \Theta(x - R_0) | \vec{\mathcal{L}} \rangle$$

Any value of A satisfying inequality (16) will produce a set of cluster levels which is a good image of the crystal bands and which does not change when changing A within this interval.

3. CONCLUSIONS

We may summarize the results of the preceding section by saying that the Brescansin and Ferreira procedure is the only cluster approach for representing an infinite crystal, whose justification goes beyond the purely intuitive arguments. In this paper we derive the necessary conditions that a cluster must satisfy in order to reproduce accurately the main crystal features. We have also shown that, if such conditions are met, the charge density around the inner cluster atoms is the same as the charge density around each atom in the crystal. The cluster energy spectrum then becomes a true image of the crystal bands, the discrete cluster levels lying between the band maximum and minimum. Moreover, we can assure that no surface state arises in such a cluster energy spectrum. We can also conclude that, if such necessary conditions are satisfied, the accuracy in the cluster results depends more on the accuracy of the quantum chemistry method used in the solution of Schrödinger and Poisson equations than in the cluster approximation.

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RESUMO

Um formalismo matemático foi desenvolvido de tal modo a determinar as condições necessárias que um pequeno agregado de átomos deve satisfazer para reproduzir com precisão as principais características da estrutura eletrônica de um cristal infinito. Mostrou-se que se tais condições forem satisfeitas a estrutura de bandas de energia do agregado será uma imagem fiel daquela do cristal. Foi mostrado, também, que quanto maiores forem as larguras das bandas proibidas no cristal, menores serão os agregados necessários para reproduzir sua estrutura de bandas.