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Electron density of periodic systems derived from non-orthogonal localized orbitals

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Abstract

Development of a quantum cluster embedding scheme based on non-orthogonal localized orbitals requires an efficient numerical method for calculating the electron density of the reference periodic crystal. We demonstrate that an existing method due to Löwdin based on the inverse overlap matrix expansion can only be used when the orbitals are highly localized (e.g. ionic systems). In other cases including covalent crystals or those with an intermediate type of chemical bonding this method may be either numerically inefficient or fail altogether. Instead, we suggest an exact and numerically efficient method which can be used for orbitals of practically arbitrary localization. Theory is illustrated by numerical calculations on a model system.

1. Introduction

Understanding of the electronic structure of extended systems with a local perturbation, e.g. point defects in the crystal bulk [1] or adsorption of molecules at crystal surfaces [2], is of fundamental importance in solid state physics and chemistry. One way of calculating the electronic structure of the above mentioned systems is based on the usage of so-called cluster methods in which a finite fragment of an extended system (a quantum cluster) is considered in detail while the rest of the system is treated at a lower level of theory [3–13]. The main problem of any existing cluster based scheme is in choosing an appropriate termination of the cluster. Usually, the quantum cluster is surrounded by point charges [5], pseudoatoms (see, e.g. [13]), link atoms [8, 6, 9] or pseudopotentials [14, 15, 13]. In more sophisticated methods the environment region is described by an electronic wavefunction which could be either frozen [10, 16] or recalculated self-consistently with that of the quantum cluster region [17, 6, 18–20] (a general theory of cluster embedding which comprises most of the existing cluster schemes is considered in [3, 4]).

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A rather general cluster method based on overlapping (not orthogonal) localized molecular orbitals is currently being developed in our laboratory. Our method, which is similar in spirit to some one-electron methods [16, 20, 19], is based on a construction of strongly localized orbitals which are designed to represent the true electronic density of the entire system via a combination of elementary densities associated in simple cases with atoms, ions and/or bonds; these are called *regions* [21]. Our intention is to create a technique which can be valid for systems of different chemical character, ranging from purely ionic to strongly covalent (excluding metals).

In addition to this, any electronic structure method requires the calculation of the electron density of the entire system from the corresponding molecular orbitals at every electronic iteration. This calculation is straightforward if the molecular orbitals are orthogonal. However, if these are not, then the calculation is not at all trivial as far as extended systems, such as crystals, are concerned. Therefore, a general and numerically efficient method of calculating electron density from a given set of strongly localized non-orthogonal orbitals localized within corresponding regions is also required.

The issue of calculating orbitals localized in appropriate regions for extreme cases of strongly ionic and covalent crystals has been considered separately [21]. It is the main objective of this paper to discuss methods of calculating the electron density of periodic systems described via localized non-orthogonal molecular orbitals.

It should be mentioned that literature on this topic is quite scarce, which is probably explained by the lack of interest (until recently) in non-orthogonal (non-canonical) molecular orbitals: in most techniques used in the solid state community, orthogonal Bloch functions are employed in practical calculations. There are only a few exceptions (see e.g. [22]). If a set of non-orthogonal molecular orbitals is used, the expression for the electron density is much more complicated since it contains an inverse of an infinite overlap matrix constructed out of the non-orthogonal orbitals of the whole system under consideration [23].

As far as we are aware, there have only been two methods developed which enable calculation of the electron density of a periodic system from non-orthogonal orbitals. Both methods are based on a series expansion of the density: while the first method [22] relies on the so-called cluster expansion of the density, the second one [24–26] is based on the power expansion of the inverse overlap matrix. In this paper we analyse only the second of the methods in detail since the first one is very complicated and much more difficult to implement. In section 2 we re-examine the second method from the point of view of the correct density normalization. Then, we suggest an alternative technique which does not require any series expansion. The two methods are compared in section 3 using a very simple model system. The paper is finished with a short discussion and conclusions in section 4.

2. Electron density of a periodic system

Let capital letters A, B etc be used to indicate regions, while the corresponding small letters a, b etc indicate localized orbitals associated with them, i.e. $a \in A, b \in B$ etc; see figure 1. Each region may have several localized orbitals. We assume that the orbitals are real. They are expanded over atomic orbitals centred only on atoms which are inside the region border. Two localized orbitals belonging to different regions are not orthogonal either because they have common atomic orbitals or, if they do not, then due to their exponential tails.

Each region A is prescribed with an even number N_A of electrons. Thus, there are a finite number $n_A = N_A/2$ of doubly occupied orbitals associated with the given region A . The localized orbitals $\varphi_{Aa}(\mathbf{r})$ belonging to the same region are assumed to be orthonormal; orbitals belonging to different regions are not orthogonal, i.e. the corresponding overlap

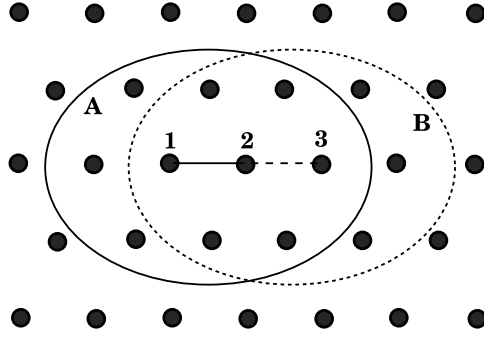


Figure 1. A schematic diagram of a division of a crystal into overlapping regions. Each atom (shown by small black circles) provides a set of atomic orbitals centred on it. Only two neighbouring regions *A* (solid line) and *B* (dashed line) are shown, which physically represent bonds between atoms 1–2 and 2–3, respectively. All atomic orbitals centred on atoms within each region contribute to the localized orbitals associated with this region. It is thus seen that different regions may have common atomic orbitals if their borders overlap. In particular, atomic orbitals of atoms 1, 2 and 3 belong to both regions indicated.

integral $S_{Aa,Bb} = \langle \varphi_{Aa} | \varphi_{Bb} \rangle$ is assumed to be not zero in general. Note that there might be several regions within every primitive unit cell in the crystal. Localized orbitals belonging to physically equivalent regions in different unit cells are obtained by appropriate lattice translations, i.e. $\varphi_{Ba}(\mathbf{r}) = \varphi_{Aa}(\mathbf{r} - \mathbf{L})$, where physically equivalent regions *B* and *A* are separated by the translation vector \mathbf{L} .

In general, the spinless electron density takes on the following general form:

$$\tilde{\rho}(\mathbf{r}, \mathbf{r}') = 2 \sum_{Aa} \sum_{Bb} \varphi_{Aa}(\mathbf{r}) (\mathbf{S}^{-1})_{Aa,Bb} \varphi_{Bb}(\mathbf{r}') \quad (1)$$

which contains the inverse of the overlap matrix, $\mathbf{S} = \|S_{Aa,Bb}\|$. The overlap matrix can also be written as a set of finite matrix blocks $\mathbf{S}_{AB} = \|S_{Aa,Bb}\|$ associated with every pair of regions. Note that for an infinite crystal the matrix \mathbf{S} has an infinite size. As usual, the factor of two is due to the fact that each orbital is occupied by two electrons with opposite spins.

In both summations above, localized orbitals from all unit cells are taken into account. To stress the periodic symmetry of the crystal, it is useful to rewrite the density in a slightly different form:

$$\tilde{\rho}(\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{L}} \rho(\mathbf{r} - \mathbf{L}, \mathbf{r}' - \mathbf{L}) \quad (2)$$

where we introduced a *periodic image* of the density ('density image' for short):

$$\rho(\mathbf{r}, \mathbf{r}') = 2 \sum'_{Aa} \sum_{Bb} \varphi_{Aa}(\mathbf{r}) (\mathbf{S}^{-1})_{Aa,Bb} \varphi_{Bb}(\mathbf{r}') \quad (3)$$

where in the first sum (indicated by a prime) the summation is run only over localized orbitals within the single primitive cell associated with the zero lattice translation; the other summation runs over all orbitals in the whole infinite system. Note that the density image is normalized on the number of electrons in the unit cell only:

$$\int \rho(\mathbf{r}, \mathbf{r}) d\mathbf{r} = \sum'_{A} N_A. \quad (4)$$

2.1. Method based on the expansion of the inverse of the overlap matrix

Following the original prescription by Löwdin [24], we present the overlap matrix as $\mathbf{S} = \mathbf{1} + \mathbf{\Delta}$, where the matrix $\mathbf{\Delta} = \|\Delta_{Aa,Bb}\|$ is the same as the original overlap matrix except for its elements when $A = B$ which are all equal to zero, $\Delta_{Aa,Aa'} = 0$. Then, one can formally write a matrix expansion:

$$\mathbf{S}^{-1} = (\mathbf{1} + \mathbf{\Delta})^{-1} = \mathbf{1} - \mathbf{\Delta} + \mathbf{\Delta}^2 - \mathbf{\Delta}^3 + \dots \quad (5)$$

One can show (using diagonalization of the matrix \mathbf{S} or its expansion over the eigenstates) that the expansion (5) can only be used if absolute values of *all* eigenvalues of the matrix $\mathbf{\Delta}$ are less than unity.

Using expansion of equation (5), one obtains the following expansion for the image density (3):

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{n=0}^{\infty} \rho^{(n)}(\mathbf{r}, \mathbf{r}') = \sum_{n=0}^{\infty} (-1)^n \left[2 \sum'_{Aa} \sum_{Bb} \varphi_{Aa}(\mathbf{r}) (\mathbf{\Delta}^n)_{Aa,Bb} \varphi_{Bb}(\mathbf{r}') \right]. \quad (6)$$

Note that a general n th-order term (for $n \geq 2$) contains an additional $n - 1$ summations over all regions due to matrix multiplications in $\mathbf{\Delta}^n$.

In principle, formulae (2) and (6) allow an approximate calculation of the electron density by terminating the infinite expansion. Care should be taken, however, in doing so to preserve the correct normalization of the density.

The zero-order contribution

$$\rho^{(0)}(\mathbf{r}, \mathbf{r}') = 2 \sum'_{Aa} \varphi_{Aa}(\mathbf{r}) \varphi_{Aa}(\mathbf{r}') \quad (7)$$

does not contain overlap integrals at all and is normalized to the total number of electrons in the unit cell. Therefore, if any higher order terms are kept in the terminated expansion (6), they should be integrated (normalized) to zero. Consider this point in more detail.

The first-order contribution to the image density

$$\rho^{(1)}(\mathbf{r}, \mathbf{r}') = -2 \sum'_{Aa} \sum_{Bb} \varphi_{Aa}(\mathbf{r}) \Delta_{Aa,Bb} \varphi_{Bb}(\mathbf{r}') \quad (8)$$

contains different regions $A \neq B$ and thus its contribution to the charge (or normalization) becomes

$$\Delta N^{(1)} = \int \rho^{(1)}(\mathbf{r}, \mathbf{r}) d\mathbf{r} = -2 \sum'_{Aa} \sum_{Bb} \Delta_{Bb,Aa} \Delta_{Aa,Bb} = -2 \sum_A \text{Tr}_A(\mathbf{\Delta}^2) \quad (9)$$

where the trace $\text{Tr}_A(\dots)$ here is calculated with respect to the localized orbitals belonging to region A only. We see that the first-order term has a finite non-zero charge (in fact, it is negative).

Any higher order contributions in equation (6) for $n \geq 2$ contain additional summations over regions, so equal regions $A = B$ in the double summation there are also possible. Therefore, every such contribution, $\rho^{(n)}(\mathbf{r}, \mathbf{r}')$, will be split into two terms: a diagonal term

$$\rho_d^{(n)}(\mathbf{r}, \mathbf{r}') = 2(-1)^n \sum'_{Aa,a'} \varphi_{Aa}(\mathbf{r}) (\mathbf{\Delta}^n)_{Aa,Aa'} \varphi_{Aa'}(\mathbf{r}') \quad (10)$$

in which $A = B$; and a non-diagonal term

$$\rho_{\text{nd}}^{(n)}(\mathbf{r}, \mathbf{r}') = 2(-1)^n \sum'_{Aa} \sum_{B(\neq A),b} \varphi_{Aa}(\mathbf{r}) (\mathbf{\Delta}^n)_{Aa,Bb} \varphi_{Bb}(\mathbf{r}') \quad (11)$$

associated with $A \neq B$ in equation (6). Correspondingly, we obtain the following contributions to the charge:

$$\Delta N_d^{(n)} = 2(-1)^n \sum'_{Aa a'} (\Delta^n)_{Aa, Aa'} S_{Aa, Aa'} = 2(-1)^n \sum'_A \text{Tr}_A(\Delta^n) \quad (12)$$

$$\Delta N_{nd}^{(n)} = 2(-1)^n \sum'_A \sum_{B(\neq A), b} (\Delta^n)_{Aa, Bb} \Delta_{Bb, Aa} = 2(-1)^n \sum'_A \text{Tr}_A(\Delta^{n+1}). \quad (13)$$

Thus, we see that for any order $n \geq 2$ we have $\Delta N_{nd}^{(n)} \equiv -\Delta N_d^{(n+1)}$. This means that the non-diagonal contribution to the density (11) is compensated exactly by the diagonal one (10) of the next order. For instance, the non-zero charge (9) is to be exactly eliminated by a charge due to the diagonal second-order density; in turn, a non-zero charge due to non-diagonal second-order density is compensated exactly by the diagonal third-order density contribution and so on.

This result is very useful since it allows one to balance properly a terminated expansion for the image density so that it would correspond (in any order!) to the correct total charge. To do this, the final expression for the density of any n th order should also include the diagonal ($A = B$) term from the contribution of the next order. We stress that this fact was ignored in the previous applications of this method [25, 26]. We obtain that the correct n th-order expansion for the image density in the notation of equations (10), (11) should have the form

$$\rho(\mathbf{r}, \mathbf{r}') \simeq \rho^{[n]}(\mathbf{r}, \mathbf{r}') \equiv \sum_{i=0}^n \left[\rho_d^{(i)}(\mathbf{r}, \mathbf{r}') + \rho_{nd}^{(i)}(\mathbf{r}, \mathbf{r}') \right] + \rho_d^{(n+1)}(\mathbf{r}, \mathbf{r}'). \quad (14)$$

Employing this termination of the series, the normalization condition (4) is satisfied exactly.

Thus, in order to calculate the density up to the n th order, one has to calculate the matrix elements $(\Delta^k)_{Aa, Bb}$ of the matrix Δ for all powers $k = 1, \dots, n$; in addition, one also needs diagonal $A = B$ elements of Δ^{n+1} . Then, the contributions from all density images corresponding to all lattice translations, equation (2), are to be added together to get the final electron density.

The method described here relies on the convergence of the density expansion (6). Better localization of the orbitals $\varphi_{Aa}(\mathbf{r})$, faster convergence and thus a smaller number of terms are needed. We shall demonstrate in section 3 that in some cases of not very well localized orbitals one has to consider the density expansion up to a very high order, which makes the calculation extremely time-consuming. Moreover, if the orbital localization becomes worse than a certain criterion (to be discussed in section 3), then this method fails altogether, as the expansion diverges. A general and an extremely efficient technique which is not based on a perturbative expansion of any kind and can be used for localized orbitals of practically any degree of localization is suggested in the next subsection.

2.2. Method based on the Fourier transform of localized orbitals

In equation (1) for the electron density, regions A and B are to be chosen from all unit cells of the infinite periodic system. It is convenient in this section to identify explicitly the lattice vector for every localized orbital in its index. Therefore, in the following we shall use letters A , B etc only for regions within the zeroth unit cell; in particular, the orbital $\varphi_{Aa}(\mathbf{r})$ is assumed to be from the zeroth cell. Localized orbitals from other cells are characterized by the combined index $(\mathbf{L}Aa)$; i.e. $\varphi_{\mathbf{L}Aa}(\mathbf{r}) = \varphi_{Aa}(\mathbf{r} - \mathbf{L})$ is the a th localized orbital from region A in the unit cell separated from the zeroth cell by the lattice translation \mathbf{L} .

Correspondingly, equation (1) is rewritten in the following way:

$$\tilde{\rho}(\mathbf{r}, \mathbf{r}') = 2 \sum_{\mathbf{L}Aa} \sum_{\mathbf{M}Bb} \varphi_{Aa}(\mathbf{r} - \mathbf{L})(\mathbf{S}^{-1})_{\mathbf{L}Aa, \mathbf{M}Bb} \varphi_{Bb}(\mathbf{r}' - \mathbf{M}) \quad (15)$$

where \mathbf{L} and \mathbf{M} are two lattice translations. A further transformation is possible here since the overlap integral $S_{\mathbf{L}Aa,\mathbf{M}Bb}$ depends in fact only on the difference $\mathbf{M} - \mathbf{L}$ of the lattice translations. This allows expansion of the overlap integral into the Fourier integral

$$S_{\mathbf{L}Aa,\mathbf{M}Bb} = \frac{1}{N} \sum_{\mathbf{k}} S_{Aa,Bb}(\mathbf{k}) e^{-i\mathbf{k}(\mathbf{L}-\mathbf{M})} \quad (16)$$

where the summation is performed over N points \mathbf{k} in the first Brillouin zone (BZ) and

$$S_{Aa,Bb}(\mathbf{k}) = \sum_{\mathbf{L}} S_{0Aa,\mathbf{L}Bb} e^{i\mathbf{k}\mathbf{L}} \quad (17)$$

is the corresponding Fourier image. The direct lattice summation in the last formula is easily terminated due to (usually) exponential decay of the overlap integrals of localized orbitals.

Using the Fourier representation of the overlap matrix, one can exactly calculate its inverse as follows:

$$(\mathbf{S}^{-1})_{\mathbf{L}Aa,\mathbf{M}Bb} = \frac{1}{N} \sum_{\mathbf{k}} [\mathbf{S}^{-1}(\mathbf{k})]_{Aa,Bb} e^{-i\mathbf{k}(\mathbf{L}-\mathbf{M})}. \quad (18)$$

Note that the matrix $\mathbf{S}(\mathbf{k}) = \|S_{Aa,Bb}(\mathbf{k})\|$ has the finite size of the number of localized orbitals per unit cell. Therefore, in order to calculate the inverse of the overlap matrix in direct space, one has to perform the calculation of $\mathbf{S}^{-1}(\mathbf{k})$ for finite size matrices for every \mathbf{k} point necessary to sample the BZ. Substituting equation (18) into (15), we arrive at the following final expression for the electron density:

$$\tilde{\rho}(\mathbf{r}, \mathbf{r}') = \frac{2}{N} \sum_{\mathbf{k}} \left\{ \sum_{Aa} \sum_{Bb} \varphi_{Aa}(\mathbf{r}, \mathbf{k}) [\mathbf{S}^{-1}(\mathbf{k})]_{Aa,Bb} \varphi_{Bb}^*(\mathbf{r}', \mathbf{k}) \right\} \quad (19)$$

where

$$\varphi_{Aa}(\mathbf{r}, \mathbf{k}) = \sum_{\mathbf{L}} \varphi_{Aa}(\mathbf{r} - \mathbf{L}) e^{-i\mathbf{k}\mathbf{L}} \quad (20)$$

is the Fourier expansion of the localized orbital. Due to the exponential decay of the localized orbitals, the summation over lattice vectors \mathbf{L} in the last expression is in fact finite.

The formula obtained for the density is exact. In particular, it contains the periodicity of the lattice built in. It is also extremely convenient for numerical implementation. Indeed, what is needed is the calculation of the Fourier images, according to equation (20), of every localized orbital in the primitive unit cell for every \mathbf{k} point. The summations in the curly brackets in equation (19) are finite (limited to the orbitals within the zeroth cell only) and are thus easily performed. The extent to which the orbitals $\varphi_{Aa}(\mathbf{r})$ are localized is reflected by the number of cells to be taken into account while performing the lattice summations in equations (17) and (20). Even for orbitals which are not very well localized, the amount of work needed to perform these lattice summations is not comparable with the cost of the first method (section 2.1) which requires including more terms in the perturbation expansion if the localization is not good enough.

3. Results

Atomic units are used throughout this section. The application of the two methods considered in the previous sections is illustrated here on a simple cubic lattice model containing a single region in every unit cell. The lattice constant a will be assumed to be equal to 1 au for simplicity. Each region is represented by a single localized orbital in the form of a normalized s type Gaussian:

$$\varphi_{\mathbf{L}Aa}(\mathbf{r}) \rightarrow \varphi_{\mathbf{L}}(\mathbf{r}) \equiv \varphi(\mathbf{r} - \mathbf{L}), \quad \varphi(r) = \left(\frac{2\alpha}{\pi} \right)^{3/4} e^{-\alpha r^2}. \quad (21)$$

By choosing various values for the exponent α , one can vary the degree of localization of the orbitals. Indeed, the size of the *spatial extent* of the orbital can be measured in terms of $r_{\text{eff}} = \sqrt{\frac{\ln 10}{\alpha}} \simeq 1.52\alpha^{-1/2}$, which corresponds to $e^{-\alpha r_{\text{eff}}^2} = 0.1$. We found this approach more convenient in our particular case than the application of the existing localization criterion (see, e.g., [27, 28]).

For this model system it is possible to do some preliminary analytical estimations of the convergence of the series (5). We know from section 2.1 that the series will converge if *all* eigenvalues Δ_λ of the matrix $\Delta = \mathbf{S} - \mathbf{1}$ are between -1 and 1 . It is easy to see that the eigenvalues are in fact given by the Fourier transforms $\Delta_{\mathbf{k}}$ of the matrix Δ which is introduced much in the same way as $\mathbf{S}(\mathbf{k})$ in equation (17). Indeed, because $\Delta_{\mathbf{L},\mathbf{M}} = \Delta_{\mathbf{0},\mathbf{M}-\mathbf{L}}$, one can write

$$\sum_{\mathbf{M}} \Delta_{\mathbf{L},\mathbf{M}} e^{i\mathbf{k}\mathbf{M}} = \left(\sum_{\mathbf{M}} \Delta_{\mathbf{0},\mathbf{M}-\mathbf{L}} e^{i\mathbf{k}(\mathbf{M}-\mathbf{L})} \right) e^{i\mathbf{k}\mathbf{L}} = \Delta_{\mathbf{k}} e^{i\mathbf{k}\mathbf{L}}. \quad (22)$$

This is nothing but the eigenproblem for the matrix Δ with $\Delta_{\mathbf{k}}$ being its eigenvalues (numbered by vectors \mathbf{k} from the BZ) and $\|e^{i\mathbf{k}\mathbf{L}}\|$ its eigenvectors. Therefore, the convergence criterion for the series (5) reduces to the inequalities $|\Delta_{\mathbf{k}}| < 1$ which should be valid for *any* \mathbf{k} . Taking into account the overlap only between nearest neighbours, we obtain

$$|\Delta_{\mathbf{k}}| = |2\delta(\cos(k_x a) + \cos(k_y a) + \cos(k_z a))| \leq 6\delta < 1$$

with the overlap between neighbouring orbitals being $\delta = e^{-\alpha a^2/2}$. This results in the following criterion for the convergence of the Löwdin expansion (for $a = 1$ au):

$$\alpha \geq \alpha_1^* = 2 \ln(6) \approx 3.6. \quad (23)$$

Similar analysis which takes into account the next nearest neighbours gives a very similar estimate of $\alpha_1^* \approx 4.05$. These estimates correspond to the maximum spatial extent of the orbitals (21) of the order of $r_{\text{eff}} \simeq 0.76$ au, i.e. there is very small overlap between neighbouring orbitals which, we recall, are separated by 1 au in the lattice.

The other method based on the Fourier transform of the orbitals also has its limits, which are hidden in the formulae (17) and (20): if a certain cut-off $|\mathbf{L}| \leq r_c$ for the direct lattice summation \mathbf{L} is assumed in the calculation of $S_{Aa,Bb}(\mathbf{k})$ and $\varphi_{Aa}(\mathbf{r}, \mathbf{k})$, then there will be some limitations on the allowed degree of localization of the orbitals. The required criterion can be worked out e.g. by analysing the Fourier transform (20) of the orbital at its maximum in the centre of the BZ (i.e. of $\varphi(\mathbf{r} = \mathbf{0}, \mathbf{k} = \mathbf{0})$) as follows:

$$\sum_{|\mathbf{L}| > r_c} \varphi(\mathbf{L}) \ll \sum_{|\mathbf{L}| < r_c} \varphi(\mathbf{L}).$$

Replacing the sums by the corresponding volume integrals, we obtain the following criterion:

$$x e^{-x^2} + \frac{\sqrt{\pi}}{2} \operatorname{erfc}(x) \ll \frac{\sqrt{\pi}}{4}$$

where $x = r_c \sqrt{\alpha}$. The inequality above is satisfied if $x \geq 2$, i.e. $\alpha \geq 4/r_c^2$. Assuming that r_c is equal to 4–5 lattice constants, we obtain the necessary condition for the exponent of the localized orbitals:

$$\alpha \gg \alpha_2^* \sim 0.2 \quad (24)$$

for which our Fourier transform method should work. The critical value of α_2^* obtained results in the maximum spatial extent of the orbitals of the order of $r_{\text{eff}} \simeq 3.4$ au, which corresponds to very diffuse orbitals spreading over more than six unit cells.

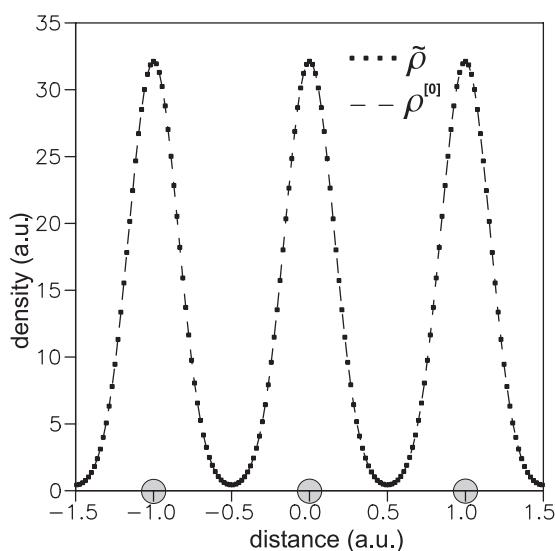


Figure 2. The exact electron density $\tilde{\rho}(r, r)$, equation (19), and that based on the zero-order approximation $\rho^{(0)}(r, r)$, equation (7), both calculated along the (100) direction using $\alpha = 10$ au. Note that the densities are nearly zero between the localization centres shown by grey circles.

A similar criterion is obtained for the overlap integrals as well. Thus, the method that we suggest should have a much wider range of applicability than the Löwdin method as far as the degree of localization of the non-orthogonal orbitals is concerned, since $\alpha_1^* \gg \alpha_2^*$. This conclusion is also supported by our numerical calculations which we now describe.

Numerical calculations of the necessary powers of the Δ matrix needed for the Löwdin method were done in the following way. Since the density is calculated at the same point $\mathbf{r} = \mathbf{r}'$ in equations (10), (11) and (14), the regions A and B in these equations are either the same or not far away from each other. Therefore, to calculate $(\Delta^n)_{Aa, Bb}$ one can simply choose a sufficiently big finite cluster of atoms (in fact, the cluster radius should be at least of the order of $\frac{n}{2}r_c^*$, where r_c^* is the decay length of the overlap integral) with regions A and B somewhere in its centre and then calculate the complete overlap matrix for it, $\tilde{\Delta}$. Then, by performing the necessary $n - 1$ matrix multiplications, one can calculate $(\Delta^n)_{Aa, Bb}$ as $(\tilde{\Delta}^n)_{Aa, Bb}$.

When using the Fourier transform method, we employed the Monkhorst–Pack (MP) method [29] for the \mathbf{k} point sampling and the same cut-off distance for the direct lattice summations in equations (17) and (20) as in the previous method. In all our calculations we used the $4 \times 4 \times 4$ MP set which was found to be sufficient in all cases.

Results of our calculations for a large value of the exponent ($\alpha \gg \alpha_1^* \gg \alpha_2^*$) are shown in figure 2. This case corresponds to strongly localized orbitals as is the case in ionic systems such as MgO and NaCl. Overlap between orbitals is negligible and even the zero-order approximation Löwdin method, equation (7), was found sufficient to give the correct density. Density curves for the two methods are indistinguishable from each other.

The calculated densities in the intermediate case ($\alpha \sim \alpha_1^*$) are shown in figure 3. This value of α may correspond to ion–covalent and covalent systems. One can see that high order approximations (up to $n = 8$) of the Löwdin method, equation (14), are needed here to converge the density and thus the calculation is quite time-consuming.

Finally, we show in figure 4 the densities calculated using both methods for orbitals which are least localized when $\alpha_1^* > \alpha > \alpha_2^*$. The density, obtained using the Fourier transform method, equation (19), is spread almost uniformly in the crystal volume and thus may correspond to a metallic band. At the same time, the Löwdin expansion method, equation (14), does not converge at all and the density is clearly diverges.

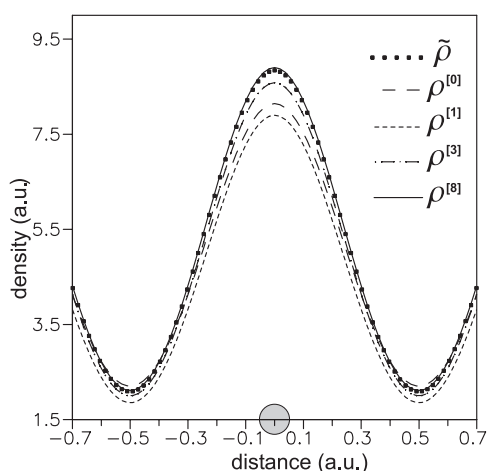


Figure 3. The exact electron density $\tilde{\rho}(r, r)$, equation (19), and the several approximations to it using equation (14) with $n = 0, 1, 3$ and 8 , all calculated along the (100) direction using $\alpha = 4$ au. Note that the density is small (but non-zero) between the localization centres.

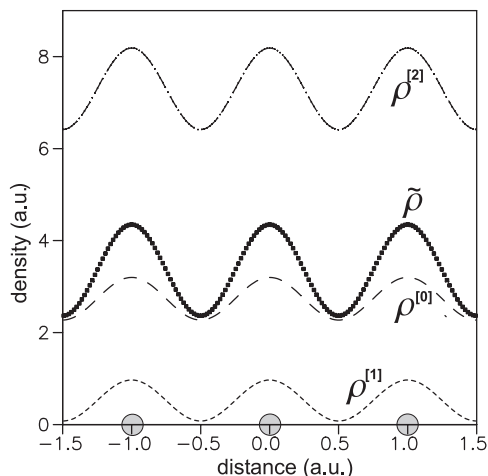


Figure 4. The electron densities for $\alpha = 2$ au. The other notation is the same as in figure 3. Note that the correct density (dots) is rather large between the localization centres.

One can expect the latter situation to happen only for metallic systems. Interestingly, our calculations (not reported here) for such a realistic covalent system as crystalline Si show that the Löwdin approach also fails in some cases when the orbitals are not sufficiently localized. Note that various degrees of localization of the orbitals can be obtained using different localization techniques and different choices of regions; see [21] for more details.

4. Conclusions

In summary, we have considered two numerical methods which allow calculation of the electron density of a 3D periodic system constructed via a set of non-orthogonal molecular localized orbitals. The first, so-called Löwdin, method based on the power expansion of the inverse of the overlap matrix has been found to be efficient only for strongly localized orbitals. For an intermediate degree of orbital localization this method has been found to be quite computationally demanding, since many terms in the series are to be retained. However, if orbitals are not sufficiently localized (the exact criterion has also been suggested), the method fails altogether and the power expansion has been shown to be divergent.

Then, we have suggested another method based on the Fourier transform of the localized orbitals which involves calculations of inverses of only finite matrices and a \mathbf{k} point summation over the Brillouin zone. This method is computationally much less demanding and does not have any convergence problems. Using a simple model for the crystal electron density represented via a set of Gaussian s type orbitals in a simple cubic lattice (one orbital per unit cell), we have shown that our method works equally well within a rather wide range of orbitals having different localization, whereas the first method fails for a relatively weakly localized orbitals. The application of the Fourier transform method to realistic systems such as MgO and Si perfect crystals is published elsewhere [21].

The method suggested here is to be used in the cluster embedding method which is currently being developed in our laboratory to represent a link with the environment region surrounding the quantum cluster.

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