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Symmetric orthogonalisation in momentum space: A numerical study

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Summary. Symmetric orthogonalisation is favourable to perform in momentum space, as this article will show. We have used a model of a body centered cubic lattice with 1*s*- and 2*s*-Slater orbitals centered at each atom site. Computer programs have been written to calculate the eigenvalues of the overlap matrix which play an important role in constructing symmetrically orthogonalised wavefunctions.

Key words: Symmetric orthogonalisation – Momentum space

1 Introduction

Symmetric orthogonalisation [SO] was first introduced by Löwdin in 1947 [1] in his work on cohesive and elastic properties of ionic crystals. Subsequent work is summarised in a survey article from 1970 [2].

SO is particularly advantageous for solids, or in general for extended systems, as it treats all unit cells "democratically". Although it was originally developed for ionic crystals, where the overlap integrals are small, it is capable of handling also systems with large overlap integrals like those occurring in metals [3–6].

For molecules SO is a standard procedure, implicitly or explicitly, in all methods using basic functions of atomic orbital type. For solids other types of basis functions have so far been dominating, even though SO is implicitly at the basis of several methods. As shown in the reference cited, powerful methods exist for the implementation of SO in extended systems. The resulting orthogonalised atomic orbitals [OAO] are however many centered functions which makes them less attractive to work with explicitly. An alternative representation is provided by working in momentum space. By introducing the concept of reciprocal space, which is closely related to but not identical to momentum space [7, 8], difficult numerical problems that occur in position space can be avoided [9].

Even though OAO's are not calculated explicitly in methods like PPP or of "NDO" type they constitute the conceptual basis for all semiempirical procedures of that kind. This has been known for a long time, but it is nevertheless interesting to notice the recent historical paper by Parr [10] in which a handwritten letter

from Löwdin is reproduced. More about the justification of the "zero differential overlap" approximation can be found in a survey paper by Fischer-Hjalmars [11] as well as in papers quoted in [10]. In solid state theory the Hubbard model [12] plays an extremely important part and since it constitutes a special case of the PPP model [13] the aspects of SO discussed in the present paper should be of interest also for the Hubbard model.

SO of a set of AO's can be regarded as a kind of "renormalisation" of their counterparts in momentum space [9]. All that is required are the eigenvalues $d(\boldsymbol{k})$ of the overlap matrix in the first Brillouin zone [BZ]. In order to make SO really attractive we thus need a simple and powerful procedure for calculating these eigenvalues from the AO's. In the present paper we study the merits and/or the disadvantages of two procedures developed for that purpose. The traditional one uses the explicit overlap integrals of the AO's and works entirely in position space. The other one works in momentum space and uses only the values of the momentum space counterparts of the AO's. As detailed below we study primarily convergence questions and some practical computational problems. The eigenvalues of the overlap matrix play an important role, particularly the smallest one of them, in its capacity as a measure of linear dependence [14]. A numerical study for related problems has been published [15]. In the present paper we will introduce an alternative procedure for calculating the eigenvalues of the overlap matrix, based either on expansions in momentum space or on combinations of expansions in momentum space and in position space.

As an introduction we will discuss the relevant parts of reference [9]. This section is general, but in the proceeding section, named "Numerical studies", we will specialise first to a one-dimensional lattice, part A, and then to a three-dimensional lattice, part B. The one-dimensional case is probably more penetrable to the reader than the three-dimensional one and is included for pedagogical reasons. The aim of the article is however introduced in part B where we treat a three-dimensional lattice with two Slater orbitals. All through the article we have treated the problem in position space in parallel with the problem in momentum space.

2 Eigenvalues of the overlap matrix

We start out with a brief review of the relevant parts of Ref. [9] to which the reader is referred for additional information. An orbital $\phi(\boldsymbol{r})$ in position space and its counterpart $\hat{\phi}(\boldsymbol{p})$ in momentum space are connected by means of Fourier transforms:

$$\hat{\phi}(\boldsymbol{p}) = \frac{1}{\sqrt{8\pi^3}} \int d\boldsymbol{r}\, \phi(\boldsymbol{r})\, e^{-i\boldsymbol{p}\cdot\boldsymbol{r}} \tag{1}$$

$$\phi(\boldsymbol{r}) = \frac{1}{\sqrt{8\pi^3}} \int d\boldsymbol{p}\, \hat{\phi}(\boldsymbol{p})\, e^{i\boldsymbol{p}\cdot\boldsymbol{r}} \tag{2}$$

This implies that the overlap integral in position space is identical to its counterpart in momentum space:

$$\Delta_{12} = \int d\boldsymbol{r}\, \phi_1^*(\boldsymbol{r})\phi_2(\boldsymbol{r}) = \int d\boldsymbol{p}\, \hat{\phi}_1^*(\boldsymbol{p})\hat{\phi}_2(\boldsymbol{p}) \tag{3}$$

For an orbital that is localised in position space we use either one of the notations:

$$\phi(\boldsymbol{m}, \boldsymbol{r}) = \phi(\boldsymbol{r} - \boldsymbol{m}) \tag{4}$$

where $\boldsymbol{m}$ is a direct lattice vector which also labels the unit cells. The momentum space counterpart of Eq. (4) is:

$$\hat{\phi}(\boldsymbol{m}, \boldsymbol{p}) = \hat{\phi}(\boldsymbol{p})\, e^{-i\boldsymbol{p}\cdot\boldsymbol{m}} \quad \text{with } \hat{\phi}(\boldsymbol{p}) = \hat{\phi}(0, \boldsymbol{p}) \tag{5}$$

Equation (5) illustrates how a translation in direct space simply becomes a phase factor in momentum space. A typical LCAO overlap integral can then be expressed in two equivalent ways:

$$\Delta(\boldsymbol{m}, \boldsymbol{n}) = \int dv\, \phi^*(\boldsymbol{m}, \boldsymbol{r})\phi(\boldsymbol{n}, \boldsymbol{r}) = \int d\boldsymbol{p}\, |\hat{\phi}(\boldsymbol{p})|^2\, e^{i\boldsymbol{p}\cdot(\boldsymbol{m}-\boldsymbol{n})} \tag{6}$$

These overlap integrals together form an overlap matrix Δ. If the orbitals of Eq. (4) satisfy periodic boundary conditions in the sense that $\phi(\boldsymbol{m} + G\boldsymbol{a}_i, \boldsymbol{r}) = \phi(\boldsymbol{m}, \boldsymbol{r})$, that matrix is cyclic. Here $\boldsymbol{a}_i$ is any of the three basis vectors of the direct lattice and G is the number of such vectors in each direction which determine the Born–Karman region. We also write $G^3 = N$. Δ is therefore diagonalised by the unitary matrix $\boldsymbol{U}$ with elements:

$$U(\boldsymbol{m}, \boldsymbol{k}) = \frac{1}{\sqrt{N}}\, e^{i\boldsymbol{k}\cdot\boldsymbol{m}} \tag{7}$$

where $\boldsymbol{k}$ is a wave vector in BZ and N is the number of unit cells in the Born–Karman region [BK]. Consequently the matrix:

$$\boldsymbol{d} = U^{\dagger}\Delta U \tag{8}$$

with elements:

$$d(\boldsymbol{k}) = \sum_{\boldsymbol{m},\boldsymbol{n}}^{BK} U^{\dagger}(\boldsymbol{k}, \boldsymbol{m})\Delta(\boldsymbol{m}, \boldsymbol{n})U(\boldsymbol{n}, \boldsymbol{k}) = \sum_{\boldsymbol{m}}^{BK} \Delta(\boldsymbol{m}, 0)\, e^{i\boldsymbol{k}\cdot\boldsymbol{m}} \tag{9}$$

is diagonal and these diagonal elements are the eigenvalues of Δ. Working in momentum space we get the alternative expression:

$$d(\boldsymbol{k}) = \frac{8\pi^3}{V_{0a}} \sum_{\boldsymbol{K}} |\hat{\phi}(\boldsymbol{k} + \boldsymbol{K})|^2 \tag{10}$$

where V_{0a} is the volume of the unit cell in the direct lattice and the sum is carried out over all reciprocal lattice vectors $\boldsymbol{K}$. With one orbital $\phi(\boldsymbol{r})$ per unit cell the symmetrically orthonormalised counterpart in momentum space is:

$$\hat{\varphi}(\boldsymbol{p}) = \frac{\hat{\phi}(\boldsymbol{p})}{\sqrt{d(\boldsymbol{k})}} \tag{11}$$

where $\boldsymbol{k}$ is that wave vector in BZ which is equivalent to $\boldsymbol{p}$, i.e. is related to $\boldsymbol{p}$ via a reciprocal lattice vector $\boldsymbol{K}$:

$$\boldsymbol{p} = \boldsymbol{k} + \boldsymbol{K} \tag{12}$$

If each unit cell contains several orbitals $\phi_i(r)$ $i = 1, 2, 3 \ldots$ we need for each $\boldsymbol{k}$ in BZ the matrix $\boldsymbol{D}(\boldsymbol{k})$ with elements:

$$D_{ij}(\boldsymbol{k}) = \frac{d_{ij}(\boldsymbol{k})}{\sqrt{d_{ii}(\boldsymbol{k})d_{jj}(\boldsymbol{k})}} \tag{13}$$

in order to construct completely orthonormal orbitals. Here:

$$d_{ij}(\boldsymbol{k}) = \sum_{\boldsymbol{m}} \Delta_{ij}(m, 0)\, e^{-i\boldsymbol{k}\cdot\boldsymbol{m}} = \frac{8\pi^3}{V_{0a}} \sum_{\boldsymbol{K}} \hat{\phi}_i^*(\boldsymbol{k}+\boldsymbol{K})\hat{\phi}_j(\boldsymbol{k}+\boldsymbol{K}) \tag{14}$$

and Δ_{ij} is a block of the full overlap matrix corresponding to orbitals of type i and j respectively, in all the unit cells. Throughout the present paper we work primarily with a finite Born–Karman region. Occasionally it will be advantageous, however, to go to the limit of an infinite BK.

3 Numerical studies

3.1 One-dimensional lattice

We first apply the formalism described in the previous section to a linear (cyclic) chain of atoms with Na as the length of the Born–Karman region. BZ is then in the interval:

$$-\frac{\pi}{a} \leqslant k < \frac{\pi}{a} \tag{15}$$

and the direct lattice vectors are labeled as follows:

$$\boldsymbol{m} = \mu a \boldsymbol{e}_z \qquad -\frac{N}{2} \leqslant \mu < \frac{N}{2} \tag{16}$$

We place a $1s$ Slater orbital:

$$\phi(\boldsymbol{r}) = \frac{1}{\sqrt{\pi}} e^{-r} \tag{17}$$

on each atom and proceed to calculate the eigenvalues of the corresponding overlap matrix Δ with the elements:

$$\Delta_\mu = \Delta(0, \boldsymbol{m}) = e^{-|\mu|a}[1 + |\mu|a + \tfrac{1}{3}(\mu a)^2] \tag{18}$$

In direct space we get for the eigenvalues $d(\boldsymbol{k})$ of Δ according to Eq. (9):

$$d(\boldsymbol{k}) = 1 + 2 \sum_{\mu=1}^{N/2} \Delta_\mu \cos(ak\mu) \tag{19}$$

In this particular case of the sum of Eq. (19) with Δ_μ from Eq. (18) can be summed in closed form. To see that we start out from the geometric progression:

$$\lim_{N\to\infty} \sum_{\mu=1}^{N/2} e^{-\mu a} = \lim_{N\to\infty} \frac{1 - e^{-Na/2}}{e^a - 1} = \frac{1}{e^a - 1} \tag{20}$$

Differentiating this with respect to a we get:

$$\sum_{\mu=1}^{N/2} \mu\, e^{-\mu a} = \frac{e^a}{(e^a-1)^2} \tag{21}$$

$$\sum_{\mu=1}^{N/2} \mu^2\, e^{-\mu a} = \frac{e^a(e^a+1)}{(e^a-1)^3} \tag{22}$$

This gives for $\boldsymbol{k} = 0$ the closed expression:

$$d(0) = 1 + 2\left[\frac{a^2}{3}\frac{e^a(e^a+1)}{(e^a-1)^3} + \frac{a\,e^a}{(e^a-1)^2} + \frac{1}{e^a-1}\right] \tag{23}$$

One can proceed in a similar way to get the eigenvalues for other special values of $\boldsymbol{k}$. The general result for an arbitrary $\boldsymbol{k}$ can be obtained from sums similar to Eqs. (20)–(22) from complex values of a:

$$d(k) = 1 + \frac{2(e^a\cos(ak) - 1)}{e^{2a} - 2e^a\cos(ak) + 1} + \frac{2a\,e^a(e^{2a}\cos(ak) + \cos(ak) - 2e^a)}{(e^{2a} - 2e^a\cos(ak) + 1)^2}$$
$$+ \frac{2a^2\,e^a((e^{4a}-1)\cos(ak) + e^a(2^{2a}-1)\cos(2ak) - 3e^a(e^{2a}-1))}{3(e^{2a} - 2e^a\cos(ak) + 1)^3} \tag{24}$$

For checking purposes we notice the following values obtained from Eq. (24).

Table 1

k	$a = 1$	$a = 2$	$a \to \infty$
0	5.333496	2.670909	1
π/a	0.008322	0.128387	1

We compare these numbers with the results of partial sums of Eq. (19) for finite values of N:

Table 2

N	k	$a = 1$	$a = 2$	N	k	$a = 1$	$a = 2$
2	0	2.71676	2.17290	2	π/a	−0.71676	−0.17290
4	0	3.88966	2.55143	4	π/a	0.45614	0.20563
6	0	4.58668	2.64564	6	π/a	−0.24088	0.11142
8	0	4.96522	2.66596	8	π/a	0.13766	0.13175
10	0	5.15838	2.66995	10	π/a	−0.05550	0.12776
12	0	5.25258	2.67068	12	π/a	0.03870	0.12849
14	0	5.29696	2.67081	14	π/a	−0.00568	0.12836
16	0	5.31728	2.67083	16	π/a	0.01464	0.12838
18	0	5.32640	2.67084	18	π/a	0.00552	0.12838
20	0	5.33040	2.67084	20	π/a	0.00952	0.12838
22	0	5.33218	2.67084	22	π/a	0.00744	0.12838
24	0	5.33292	2.67084	24	π/a	0.00848	0.12838

In momentum space we cannot use Eq. (10) since we have imposed periodic boundary conditions only in one dimension (z). Momentum space is therefore discretised only in the p_z direction, i.e. momentum space functions are different from zero only for:

$$p_z = \frac{2\pi v}{Na} \quad v = 0, \pm 1, \pm 2 \ldots \tag{25}$$

The Fourier transform of Eq. (17) is:

$$\hat{\phi}_{1s}(\boldsymbol{p}) = \sqrt{\frac{8}{\pi^2}} \frac{1}{(p^2+1)^2} \tag{26}$$

so that Eq. (10) becomes:

$$d(k) = \sum_{\mu=-N/2}^{N/2-1} e^{-ik a\mu} \int d\boldsymbol{p}\, |\hat{\phi}(\boldsymbol{p})|^2\, e^{ip_z \mu a} = \frac{16}{3a} \sum_{\nu=-\infty}^{\infty} \frac{1}{\left[1+\left(k+\frac{2\pi\nu}{a}\right)^2\right]^3} \tag{27}$$

In Table 3 we show the "convergence rate" of this formula for the same values of a and k as in Tables 1 and 2. As can be expected the momentum space sum converges more rapidly than the one in position space, particularly for $a = 1$.

Table 3

N	k	$a=1$	$a=2$
1	0	5.333333	2.666667
3	0	5.333494	2.670819
5	0	5.333497	2.670900
7	0	5.333497	2.670907
9	0	5.333497	2.670908
2	π/a	0.009306	0.127934
4	π/a	0.008321	0.128360
6	π/a	0.008321	0.128382
8	π/a	0.008321	0.128385
10	π/a	0.008321	0.128386

3.2 Three-dimensional lattice

We then go to a three-dimensional solid with a body centered cubic (bcc) lattice. With a lattice constant (cube edge) of a the bcc lattice is characterised by the following lattice point:

$$\frac{a}{2}(2k, 2l, 2m) \quad \text{and} \quad \frac{a}{2}(2k+1, 2l+1, 2m+1) \quad k, l, m = 0, \pm 1, \pm 2 \ldots \tag{28}$$

The unit cell volume V_{0a} is $a^3/2$. The properties of the neighbours up to order eight are summarised in Table 4 and Fig. 1. Thus inclusion of all neighbours up to order eight in a lattice sum corresponds to 112 neighbours.

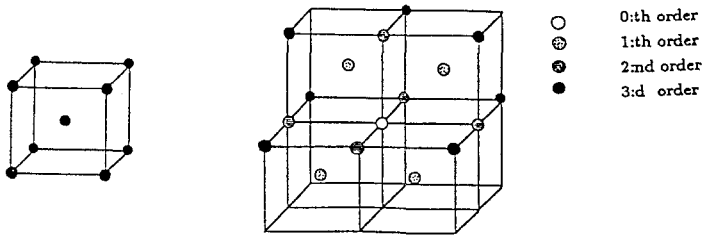

Fig. 1

Table 4

Coordinates $a/2$	Order	Distance a	No. of neighbours
$(0, 0, 0)$	0	0	1
$(\pm1, \pm1, \pm1)$	1	$\sqrt{3}/2$	8
$(\pm2, 0, 0)$	2	1	6
$(\pm2, \pm2, 0)$	3	$\sqrt{2}$	12
$(\pm3, \pm1, \pm1)$	4	$\sqrt{11}/2$	24
$(\pm2, \pm2, \pm2)$	5	$\sqrt{3}$	8
$(\pm4, 0, 0)$	6	2	6
$(\pm3, \pm3, \pm1)$	7	$\sqrt{19}/2$	24
$(\pm4, \pm2, 0)$	8	$\sqrt{5}$	24

In general overlap integrals of the type of Eq. (6) depend both on the relative direction of $\boldsymbol{m}$ and $\boldsymbol{n}$ on the distance $|\boldsymbol{m}-\boldsymbol{n}|$. Here we will limit ourselves to s-orbitals to that $\Delta(\boldsymbol{m}, \boldsymbol{n})$ will depend only on the distance $|\boldsymbol{m}-\boldsymbol{n}|$. Lattice sums of the type (9) or (10) can then be written as follows:

$$d(\boldsymbol{k}) = \sum_{\boldsymbol{m}}^{BK} \Delta(m, 0)\, e^{-i\boldsymbol{k}\cdot\boldsymbol{m}} = \Delta(m_0, 0)\, e^0 + \Delta(m_1, 0) \sum_{\boldsymbol{m}_1} e^{-i\boldsymbol{k}\cdot\boldsymbol{m}_1}$$

$$+ \Delta(m_2, 0) \sum_{\boldsymbol{m}_2} e^{-i\boldsymbol{k}\cdot\boldsymbol{m}_2} + \cdots = \Delta(m_0, 0) f_0 + \Delta(m_1, 1) f_1 + \Delta(m_2, 0) f_2 \ldots \tag{29}$$

Here $\Delta_i(m_i, 0)$ is the overlap integral between two neighbours of order i and the sum over m_i is carried out over the neighbours of order i (last column in Table 4). The $\boldsymbol{k}$-dependence is concentrated to the functions $f_i(\boldsymbol{k})$ which are shown in Table 5 for the neighbours up to order eight.

Table 5

$$f_0(\boldsymbol{k}) = 1$$

$$f_1(\boldsymbol{k}) = 8 \cos\frac{ak_x}{2} \cos\frac{ak_y}{2} \cos\frac{ak_z}{2}$$

$$f_2(\boldsymbol{k}) = 2[\cos ak_x + \cos ak_y + \cos ak_z]$$

$$f_3(\boldsymbol{k}) = 4[\cos ak_x \cos ak_y + \cos ak_y \cos ak_z + \cos ak_z \cos ak_x]$$

$$f_4(\boldsymbol{k}) = 8\left[\cos\frac{ak_x}{2}\cos\frac{ak_y}{2}\cos\frac{3ak_z}{2} + \cos\frac{ak_x}{2}\cos\frac{3ak_y}{2}\cos\frac{ak_z}{2} + \cos\frac{3ak_x}{2}\cos\frac{ak_y}{2}\cos\frac{ak_z}{2}\right]$$

$$f_5(\boldsymbol{k}) = 8 \cos ak_x \cos ak_y \cos ak_z$$

$$f_6(\boldsymbol{k}) = 2[\cos 2ak_x + \cos 2ak_y + \cos 2ak_z]$$

$$f_7(\boldsymbol{k}) = 8\left[\cos\frac{3ak_x}{2}\cos\frac{3ak_y}{2}\cos\frac{ak_z}{2} + \cos\frac{3ak_x}{2}\cos\frac{ak_y}{2}\cos\frac{3ak_z}{2} + \cos\frac{ak_x}{2}\cos\frac{3ak_y}{2}\cos\frac{3ak_z}{2}\right]$$

$$f_8(\boldsymbol{k}) = 4[\cos 2ak_x \cos ak_y + \cos ak_x \cos 2ak_y + \cos 2ak_y \cos ak_z$$
$$+ \cos ak_y \cos 2ak_z + \cos 2ak_z \cos ak_x + \cos ak_z \cos 2ak_x]$$

In order to work in momentum space we also need the characteristics of the face centered cubic (fcc) lattice, which is the reciprocal of the bcc lattice. For the neighbours up to order eight this is summarised in Table 6 and in Fig. 2. Thus inclusion of all reciprocal lattice vectors up to order eight corresponds to 140 terms.

Table 6. Fcc lattice

Coordinates $1/a$	Order	Distance $1/a$	No. of neighbours
$(0, 0, 0)$	0	0	1
$(\pm1, \pm1, 0)$	1	$\sqrt{2}$	12
$(\pm2, 0, 0)$	2	2	6
$(\pm2, \pm1, \pm1)$	3	$\sqrt{6}$	24
$(\pm2, \pm2, 0)$	4	$\sqrt{8}$	12
$(\pm3, \pm1, 0)$	5	$\sqrt{10}$	24
$(\pm2, \pm2, \pm2)$	6	$\sqrt{12}$	8
$(\pm3, \pm2, \pm1)$	7	$\sqrt{14}$	48
$(\pm4, 0, 0)$	8	4	6

The material so far is common for all kinds of orbitals of s-type. We now test the formalism for $1s$ and $2s$ orbitals of Slater type:

$$\phi(\boldsymbol{r})_{1s} = \frac{1}{\sqrt{\pi}} e^{-r} \tag{30}$$

$$\phi(\boldsymbol{r})_{2s} = \frac{1}{4\sqrt{6\pi}} r\, e^{-r/2} \tag{31}$$

The overlap integrals corresponding to a distance ma are [16]:

$$\Delta(1s, 1s) = e^{-ma}[1 + ma + \tfrac{1}{3}(ma)^2] \tag{32}$$

$$\Delta(2s, 2s) = e^{-ma}[1 + ma + \tfrac{4}{9}(ma)^2 + \tfrac{1}{9}(ma)^3 + \tfrac{1}{45}(ma)^4] \tag{33}$$

$$\Delta(1s, 2s) = \frac{1}{8}\frac{1}{\sqrt{3}} ma^4(1+t)^{3/2}(l-t)^{5/2}[A_3B_0 - A_2B_1 - A_1B_2 + A_0B_3] \tag{34}$$

where

$$A_k(s) = e^{-s} \sum_{\mu=1}^{k+1} \frac{k!}{s^{\mu}(k-\mu+1)!} \qquad s = \frac{ma}{2} \tag{35}$$

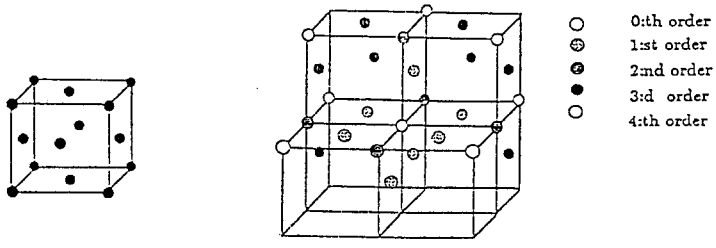

Fig. 2

and

$$B_k(s) = -e^{-st}\sum_{\mu=1}^{k+1}\frac{k!}{(st)^{\mu}(k-\mu+1)!} - e^{-st}\sum_{\mu=1}^{k+1}\frac{(-1)^{k-\mu}k!}{(st)^{\mu}(k-\mu+1)!} \tag{36}$$

where $t=\frac{1}{3}$. As pointed out in [16] the quantities A_k and B_k are preferably calculated by means of recursion formulae. For $m=0$ Eq. (35) is not valid. Direct calculation gives:

$$\int dr\, \phi^*_{1s}(r)\phi_{2s}(r) = \frac{32}{27}\frac{1}{\sqrt{6}} \tag{37}$$

The Fourier transforms of the orbitals of Eqs. (30) and (31) are:

$$\hat{\phi}_{1s}(p) = \sqrt{\frac{8}{\pi^2}}\frac{1}{(p^2+1)^2} \tag{38}$$

$$\hat{\phi}_{2s}(p) = \frac{1}{2\sqrt{3}}\frac{1}{\pi}\frac{(\frac{3}{4}-p^2)}{(\frac{1}{4}+p^2)^3} \tag{39}$$

That gives directly for the quantities of Eqs. (10) and (14):

$$d_{11}(k) = \frac{128\pi}{a^3}\sum_{K}\frac{1}{(1+(k+K)^2)^4} \tag{40}$$

$$d_{22}(k) = \frac{4\pi}{3a^3}\sum_{K}\frac{(\frac{3}{4}-(k+K)^2)^2}{(\frac{1}{4}+(k+K)^2)^6} \tag{41}$$

and

$$d_{12}(k) = \sqrt{\frac{8}{3}}\frac{8\pi}{a^3}\sum_{K}\frac{(\frac{3}{4}-(k+K)^2)}{((k+K)^2+1)^2(\frac{1}{4}+(k+K)^2)^3} \tag{42}$$

4 Results and discussion

Six different computer programs have been written. Three types of orbitals have been considered, both in position space and momentum space. For a lattice with $1s$ orbitals only, the eigenvalues in position space are given by Eqs. (29) and (32), whereas the corresponding expression in momentum space is given by Eq. (40). For a lattice with $2s$ orbitals only, we use instead Eqs. (29) and (33) in position space and Eq. (41) in momentum space. If there are both $1s$ and $2s$ orbitals we need Eqs. (29) and (34) in position space and Eq. (42) in momentum space, in order to calculate the matrix elements $d_{12}(k)$. Together with $d_{11}(k)$ and $d_{22}(k)$ these form a 2×2 matrix $D(k)$ defined in Eq. (13). That matrix raised to the power $(-1/2)$ provides the quantities needed for a complete orthonormalisation in the case when there are both $1s$ and $2s$ orbitals on each atom in the lattice.

In Tables 7–9 we show some results for different lattice constants a and different values of k. For each value of a and k we show cumulative lattice sums, Eqs. (29) and (40), (41) or (42), respectively, for an increasing number of neighbours. In all cases neighbours up to order eight have been included.

For small values of the lattice constant the sum in momentum space converges extremely quickly, whereas the sum in position space definitely needs neighbours of much higher order than eight in order to converge. For intermediate values of the lattice constant – intermediate being different for different types

Table 7. $1s1s\, d_{11}(k)$

Order of terms	Position space	Momentum space	Order of terms	Position space	Momentum space
$k_x, k_y, k_z = 0$ $a = 1$			$k_x, k_y, k_z = 0$ $a = 2$		
0	1.00000	402.12386	0	1.00000	50.26548
1	8.12034	402.12399	1	6.28223	50.26875
2	13.27065	402.12399	2	9.80095	50.26886
3	22.25882	402.12399	3	14.40772	50.26895
4	38.60020	402.12399	4	21.35798	50.26896
5	43.88243	402.12399	5	23.47747	50.26897
6	47.40115	402.12399	6	24.61304	50.26898
7	60.32968	402.12399	7	28.20278	50.26899
8	72.90554	402.12399	8	31.53062	50.26899
$k_x, k_y, k_z = 0$ $a = 5$			$k_x, k_y, k_z = 0$ $a = 10$		
0	1.00000	3.21699	0	1.00000	0.40212
1	2.21970	3.34611	1	1.04806	0.87261
2	2.79916	3.35284	2	1.06014	0.92714
3	3.05129	3.35926	3	1.06085	1.00208
4	3.24502	3.36037	4	1.06101	1.01822
5	3.29308	3.36134	5	1.06104	1.03432
6	3.30516	3.36151	6	1.06104	1.03729
7	3.32803	3.36205	7	1.06105	1.04793
8	3.34605	3.36209	8	1.06105	1.04877
$k_x, k_y, k_z = 0$ $a = 20$			$k_x, k_y, k_z = 0$ $a = 30$		
0	1.00000	0.05027	0	1.00000	0.01489
1	1.00003	0.34370	1	1.00000	0.14256
2	1.00003	0.42338	2	1.00000	0.18937
3	1.00003	0.61111	3	1.00000	0.32976
4	1.00003	0.66992	4	1.00000	0.38342
5	1.00003	0.74731	5	1.00000	0.46687
6	1.00003	0.76498	6	1.00000	0.48882
7	1.00003	0.83996	7	1.00000	0.59413
8	1.00003	0.84577	8	1.00000	0.60479

of orbitals – both the momentum and position space expressions converge relatively quickly to the same result. For very large values of the lattice constant, where the eigenvalues should approach the value one, the position space sum converges very rapidly whereas the momentum space needs more neighbours than up to order eight.

These results were to be expected and it should be possible to use them in a systematic way. By increasing the lattice constant one finds a critical value a_c such that for $a > a_c$ the position space sum converges more rapidly than the one in momentum space, whereas the reverse result is true for $a < a_c$. Suitable combinations of position and momentum sums can also be envisaged.

Table 8. $2s2s\ d_{22}(k)$

Order of terms	Position space	Momentum space	Order of terms	Position space	Momentum space
$k_x = 0.5k_y, k_z = 0 \quad a = 1$			$k_x = 0.5k_y, k_z = 0 \quad a = 2$		
0	1.00000	67.02064	0	1.00000	8.37758
1	8.67213	67.02065	1	7.74480	8.37762
2	14.34934	67.02065	2	12.56280	8.37762
3	25.07686	67.02065	3	20.06175	8.37762
4	45.66097	67.02065	4	32.73501	8.37762
5	52.40578	67.02065	5	36.43838	8.37762
6	57.22377	67.02065	6	39.02012	8.37762
7	75.49872	67.02065	7	45.42135	8.37762
8	93.60716	67.02065	8	52.39577	8.37762
$k_x = 0.5k_y, k_z = 0 \quad a = 5$			$k_x = 0.5k_y, k_z = 0 \quad a = 10$		
0	1.00000	0.53616	0	1.00000	0.06702
1	2.98686	0.53808	1	−1.57340	0.09061
2	4.73497	0.53818	2	−0.19198	0.09129
3	3.43792	0.53827	3	0.47431	0.09221
4	2.78209	0.53829	4	−0.04989	0.09245
5	0.20869	0.53830	5	0.04458	0.09271
6	1.59012	0.53830	6	0.08556	0.09275
7	−1.02004	0.53831	7	0.07722	0.09291
8	−0.13219	0.53831	8	0.10551	0.09293
$k_x = 0.5k_y, k_z = 0 \quad a = 20$			$k_x = 0.5k_y, k_z = 0 \quad a = 30$		
0	1.00000	0.00838	0	1.00000	0.00248
1	1.09447	0.26154	1	1.00611	0.08699
2	1.13545	1.04863	2	1.00733	0.38818
3	1.13289	1.11013	3	1.00733	0.55690
4	1.13267	1.11307	4	1.00733	0.58722
5	1.13212	1.12993	5	1.00733	0.91851
6	1.13217	1.12996	6	1.00733	0.92043
7	1.13214	1.13026	7	1.00733	0.94651
8	1.13215	1.13034	8	1.00733	0.97346

Equation (10) and its special cases, Eqs. (40), (41) and (42), means that we sum the squares of the absolute values of the Fourier components of the orbital in momentum space. For a given argument $\boldsymbol{k}$ of the eigenvalue of $d(\boldsymbol{k})$ we need the values of these Fourier components at points differing from $\boldsymbol{k}$ by a reciprocal lattice vector $\boldsymbol{K}$. If the reciprocal lattice constant is sufficiently large the Fourier component at the nearest neighbour is so small that its contribution to the sum vanishes. When discussing these matters one must bear in mind both the localisation properties of the orbitals as such and their localisation – in position and in momentum space – relative to the lattice under consideration. A $1s$ orbital is definietly localised in position space, which implies that its momentum

Table 9. $1s2s\ d_{12}(k)$

Order of terms	Position space	Momentum space	Order of terms	Position space	Momentum space
$k_x, k_y = 0.5,\ k_z = 0 \quad a = 1$			$k_x, k_y = 0.5,\ k_z = 0\ a = 2$		
0	0.48385	10.80930	0	0.48385	1.35116
1	4.10719	10.80930	1	3.37796	1.35074
2	6.76057	10.80930	2	5.30059	1.35073
3	11.57304	10.80930	3	7.64373	1.35072
4	20.46268	10.80930	4	10.50037	1.35072
5	23.35679	10.80930	5	11.41176	1.35072
6	25.27942	10.80930	6	11.53099	1.35072
7	32.40221	10.80930	7	11.87317	1.35072
8	39.26953	10.80930	8	11.61265	1.35071
$k_x, k_y = 0.5,\ k_z = 0 \quad a = 5$			$k_x, k_y = 0.5,\ k_z = 0 \quad a = 10$		
0	0.48385	0.08647	0	0.48385	0.01081
1	0.74883	0.06330	1	0.98621	1.23086
2	0.40258	0.06217	2	1.17752	1.22825
3	−0.22581	0.06117	3	1.20926	1.21847
4	−0.59627	0.06101	4	1.21233	1.21557
5	−0.09392	0.06088	5	1.21433	1.21258
6	0.09739	0.06085	6	1.21304	1.21201
7	0.15202	0.06079	7	1.21143	1.21002
8	−0.08258	0.06078	8	1.20915	1.20988
$k_x, k_y = 0.5,\ k_z = 0 \quad a = 20$			$k_x, k_y = 0.5,\ k_z = 0 \quad a = 30$		
0	0.48385	0.00135	0	0.48385	0.00040
1	0.48594	0.11035	1	0.48392	0.01420
2	0.48456	0.13231	2	0.48391	0.02151
3	0.48446	0.28026	3	0.48391	0.07619
4	0.48446	0.43277	4	0.48391	0.13877
5	0.48446	0.26657	5	0.48391	0.18557
6	0.48446	0.47137	6	0.48391	0.19964
7	0.48446	0.49970	7	0.48391	0.32733
8	0.48446	0.49937	8	0.48391	0.32992

space counterpart is delocalised. When the direct lattice constant is small, the reciprocal lattice constant is large. Thus even though the momentum space $1s$ orbital is delocalised, the values of it which are needed for the function $d(\boldsymbol{k})$ are to be calculated at such large values of its argument, that those values decrease very rapidly. If on the other hand the direct lattice constant is very large, the reciprocal lattice constant is very small, and the Fourier components of the delocalised function then decay very slowly.

Aissing and Monkhorst [17] have pointed out that the speed of the convergence of the overlap integral of Eq. (14) is related to the degree of linear dependence of the underlying sets of functions.

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