Perfect localized basis functions for solids: chemical pseudopotentials and the Kronig–Penney model

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Abstract. Anderson's chemical pseudopotential scheme is supposed to define a set of highly localized basis functions in terms of which the eigenstates of a solid can be expanded exactly. This sounds good in principle but little is known about the method in practice and it has not even been established that the basis functions always exist. This paper discusses some of the general properties of localized basis sets spanning a band of Bloch eigenstates and then looks at the Kronig–Penney model as an example. It is shown that the chemical pseudopotential equation has no solutions when the strength P of the attractive delta function potentials is less than about 1.4018, and that the basis functions generated are never unique when they do exist. Fortunately, it turns out that there is a generalized version of the chemical pseudopotential equation that can be solved no matter how weak the potentials, although the non-uniqueness of the basis functions remains. The solutions resemble atomic orbitals in the extreme tight-binding limit (although even then there are alternatives) but this is not true in general and so chemical pseudopotential theory should not be taken as a justification for using atomic orbitals as basis functions.

1. Introduction

Electronic structure methods based on localized basis functions have many advantages: the number of basis functions required is usually quite small; the Hamiltonian matrix is sparse; and the picture of chemical bonding that emerges is simple and intuitive. The simplicity is not surprising since chemical bonding itself is local: the Coulomb interaction is screened efficiently in most solids and so a C–H bond is much the same wherever it occurs and does not depend on the positions of distant atoms. Locality is one of the most important ideas in chemistry and explains the usefulness of simple concepts such as bond lengths and bond energies. It emerges naturally from localized basis set calculations since all the results come expressed in terms of quantities such as bond orders and orbital occupations which are themselves local [1, 2]; but in calculations using extended basis functions such as plane waves the local nature is very hard to discern. This is reflected in the structure of the Hamiltonian matrix, which is sparse in a local basis and has non-zero matrix elements only between nearby basis functions, but which is more complicated in an extended basis. Much current electronic structure work is aimed at designing $\mathcal{O}(N)$ methods [3–5] for which the calculation time scales linearly with the size of the system. This objective is attainable only because of the local nature of chemical bonding and it seems likely that successful $\mathcal{O}(N)$ methods will use localized basis functions.

The main disadvantage of using localized basis functions in solid state electronic structure calculations is the difficulty of assessing the accuracy of the basis set. In a plane

wave calculation the maximum k vector can be increased until convergence is obtained and the adequacy of the basis set is established, but analogous tests are rarely feasible when using localized basis functions. This is the problem addressed by the chemical pseudopotential method [8–16] which shows how to define optimally localized 'perfect' basis functions. They are perfect because, like Wannier functions, they can be used to expand the eigenfunctions of the solid exactly, but they are better than Wannier functions because they are more localized. The remarkable thing is that since they depend only on the local environment they can be calculated without finding all of the extended eigenfunctions of the solid first. The whole set of localized basis functions (N per unit cell) needed to span a group of N bands in the solid can therefore be calculated in a time proportional to N. The construction of the Hamiltonian matrix is also $\mathcal{O}(N)$ and dthe resulting eigenproblem is of the tight-binding type for which $\mathcal{O}(N)$ methods are already known [2, 6, 7]. There is therefore hope that the chemical pseudopotential approach could lead to a highly accurate (no basis set errors) $\mathcal{O}(N)$ electronic structure method, which would certainly be worth having.

The chemical pseudopotential basis functions are the solutions of a differential equation that looks rather like an atomic Schrödinger equation but is perturbed by weak additional potentials (the chemical pseudopotentials) due to the surrounding atoms. Unlike ordinary potentials, the chemical pseudopotentials depend on the basis functions themselves and so a form of self-consistency is required. (Note that this has nothing to do with the familiar requirement of self-consistency between the input and output potentials in Hartree–Fock and density functional calculations.) The chemical pseudopotential differential equation is difficult to solve for real solids and nobody has ever bothered to do it properly, although Anderson [12] and Hoshino *et al* [13, 14] have managed approximate solutions in particular cases. Instead, it has been argued that the chemical pseudopotentials are weak and hence that the basis functions must look very like atomic orbitals. This assumption underlies much of the work of Bullett [15], for example, but has never been properly tested. Indeed, it is not even clear that the chemical pseudopotential equation has localized solutions in all cases, never mind whether or not they look like atomic orbitals.

In this paper we first establish some of the general properties of 'perfect' basis sets of localized orbitals spanning a particular band of eigenstates in a crystal. We emphasize that the degree of localization is in one sense fixed by the shape of the bandstructure and cannot be altered: different sets of perfect basis functions may look very different, but the elements of the $\mathbf{D}$ matrix ($\mathbf{D} = \mathbf{S}^{-1}\mathbf{H}$, where $\mathbf{S}$ and $\mathbf{H}$ are the overlap and Hamiltonian matrices) are always the same. We then describe the chemical pseudopotential method and explain how it chooses one of the many possible sets of localized basis functions and how it allows those basis functions to be calculated in a local manner.

The rest of the paper concentrates on a particular example, the one dimensional Kronig–Penney model, for which most of the mathematics can be done analytically. We find that the standard version of the chemical pseudopotential equation is not soluble in the nearly free electron limit, but then show how the method may be generalized slightly to ensure that there are always solutions (for the Kronig–Penney model, at least). Surprizingly, it turns out that the solutions are never unique but always come in pairs. Both possible solutions are valid and both are localized, but one is more localized than the other. In the extreme tight-binding limit one of the two solutions tends to an atomic orbital as expected, but the other becomes a linear combination of atomic orbitals. Away from the tight binding limit neither of the solutions looks very much like an atomic orbital and so one must be very wary of general arguments invoking chemical pseudopotential theory to justify the use of atomic orbitals as basis functions.

2. General properties of perfect localized basis sets

Imagine a crystal consisting of M ($\gg 1$) unit cells altogether and subject to periodic boundary conditions. The M real space lattice vectors will be denoted by R and the reciprocal lattice vectors by G. The first Brillouin zone contains M k points consistent with the overall periodic boundary conditions. We wish to look at the properties of a set of localized basis functions, $\phi_R(r)$, spanning a particular band of eigenstates, $\psi_k(r)$. One basis function is to be centred in each unit cell and all the basis functions must be identical to within a lattice translation. There are M eigenstates in the band (one per allowed value of k in the first Brillouin zone) and we seek M localized basis functions (one for each R).

For simplicity, we will assume throughout this paper that the band in which we are interested is isolated and does not overlap any other bands. This is unlikely in a real solid, but the generalization of the theory to the case when L basis functions per unit cell span a group of L overlapping bands is fairly straightforward.

Any one of the M Bloch eigenvectors can be expanded in terms of the basis functions and symmetry tells us that the expansion coefficients must be just the usual Bloch phase factors,

$$\psi_k(r) = \frac{C(k)}{\sqrt{M}} \sum_R \exp(\mathrm{i}k \cdot R)\phi_R(r). \tag{1}$$

$C(k)$ is a normalization constant, which is not necessarily equal to unity since the basis functions need neither be normalized nor mutually orthogonal. Inverting the Fourier transform in equation (1) we find that

$$\phi_R(r) = \frac{1}{\sqrt{M}} \sum_k \exp(-\mathrm{i}k \cdot R)\frac{\psi_k(r)}{C(k)}. \tag{2}$$

If we choose $C(k) = 1$ then the localized basis functions are orthonormal and are simply the familiar Wannier functions [17, 18].

Since the set of basis functions spans a band of eigenstates it must be closed under the action of the crystal Hamiltonian, $\hat{H}$, and we can write

$$\hat{H}|\phi_R\rangle = \sum_{R'} D_{R',R}|\phi_{R'}\rangle \tag{3}$$

where $D_{R,R}$ is independent of R and $D_{R',R}$ depends only on $R' - R$ in a perfect crystal. (We are working in an independent electron formalism and so $\hat{H}$ is a Hartree–Fock or density functional Hamiltonian. Perhaps it is the Hamiltonian during one iteration of a self-consistent calculation, or perhaps it is the input Hamiltonian in a non-self-consistent Harris functional calculation [20, 21].) Taking matrix elements shows that the **D** matrix is related to the Hamiltonian and overlap matrices, **H** and **S**, via

$$H_{R'',R} = \sum_{R'} S_{R'',R'} D_{R',R}. \tag{4}$$

It is the **D** matrix, rather than the more familiar **H** and **S** matrices, that takes the central place in chemical pseudopotential theory.

In this simple translationally invariant example, the **D** matrix elements are directly related to the bandstructure $\varepsilon(k)$. If equations (1) and (3) are substituted into the Schrödinger equation

$$\hat{H}|\psi_k\rangle = \left(\hat{T} + \hat{V}\right)|\psi_k\rangle = \varepsilon(k)|\psi_k\rangle \tag{5}$$

one obtains

$$\hat{H} \sum_R \exp(i k \cdot R)|\phi_R\rangle = \sum_{R,R'} \exp(i k \cdot R) D_{R',R}|\phi_{R'}\rangle = \varepsilon(k) \sum_{R'} \exp(i k \cdot R')|\phi_{R'}\rangle \qquad (6)$$

and the linear independence of the basis functions then implies that

$$\varepsilon(k) = \sum_R \exp(-i k \cdot R') D_{R',R} \exp(i k \cdot R) = \sum_R D_{0,R} \exp(i k \cdot R) = \sum_R D_{R,0} \exp(-i k \cdot R)$$

$$(7)$$

where the last two steps made use of the translational invariance and inversion symmetry of the Bravais lattice. $\varepsilon(k)$ is a periodic function in k space and so has Fourier components corresponding to each real space lattice vector. These Fourier components are simply the **D** matrix elements which are therefore completely determined by the bandstructure and are the same no matter which of the infinitely many possible sets of localized basis functions we choose. The **H** and **S** matrices clearly depend on the details of the basis functions (whether we use orthonormal Wannier functions or non-orthonormal chemical pseudopotential basis functions, for example), but $\mathbf{D} = \mathbf{S}^{-1}\mathbf{H}$ is always the same as long as all the basis functions are identical to within a lattice translation and there is one basis function per unit cell. Anderson [10] realized this, but he also pointed out that non-orthonormal bases can consist of more localized functions than orthonormal ones. This is undoubtedly true, but the invariance of the **D** matrix makes the usefulness of the extra localization debatable. Inverting equation (7) we obtain

$$D_{0,R} = \frac{1}{M} \sum_k \varepsilon(k) \exp(-i k \cdot R) \qquad D_{R,0} = \frac{1}{M} \sum_k \varepsilon(k) \exp(i k \cdot R) \quad (8)$$

which reinforces the point that the **D** matrix is determined by the bandstructure and does not depend on the details of the basis set.

The basis functions are linear combinations of the eigenfunctions and so the Fourier components of the two sets of functions are related simply. ϕ_R may have non-zero Fourier components at any wavevector consistent with the overall periodic boundary conditions

$$\phi_R(r) = \frac{1}{M} \sum_{k,G} \bar{\phi}_R(k+G) \exp[i(k+G) \cdot r] \qquad (9)$$

where the sum over k covers all M k points in the first Brillouin zone and the sum over G extends over all the reciprocal lattice vectors. The normalized Bloch eigenfunctions ψ_k have Fourier expansions of the form

$$\psi_k(r) = \frac{1}{\sqrt{M}} \sum_G \bar{\psi}_k(k+G) \exp[i(k+G) \cdot r]. \qquad (10)$$

Note that the Fourier components of ψ_k are non-zero only at wavevectors differing from k by reciprocal lattice vectors and so cover a much coarser grid in reciprocal space than do the Fourier components of ϕ_R. The relation between the two Fourier expansions is obtained by substituting both into equation (2) and the result is

$$\bar{\phi}_R(k+G) = \frac{\bar{\psi}_k(k+G)}{C(k)} \exp(-i k \cdot R). \qquad (11)$$

The Fourier components of the eigenfunctions satisfy the Schrödinger equation in reciprocal space

$$\frac{1}{2}|k + G|^2 \bar{\psi}_k(k + G) + \sum_{G'} \bar{V}(G')\bar{\psi}_k(k + G - G') = \varepsilon(k)\bar{\psi}_k(k + G) \tag{12}$$

where

$$V(r) = \sum_G \bar{V}(G)\exp(\mathrm{i}G \cdot r). \tag{13}$$

Equation (12) fixes the relative magnitudes of the Fourier components of the eigenfunctions at all points on the coarse reciprocal space mesh of points $k + G$ with k fixed and G any reciprocal lattice vector, but equation (11) shows that at all points on this grid, $\bar{\phi}_R$ is simply a constant multiple of $\bar{\psi}_k$ (the multiplier depends on k but not on G and so really is the same at all the grid points). Hence the Fourier components of ϕ_R satisfy exactly the same reciprocal space Schrödinger equation as the Fourier components of the eigenfunctions

$$\frac{1}{2}|k + G|^2 \bar{\phi}_R(k + G) + \sum_{G'} \bar{V}(G')\bar{\phi}_R(k + G - G') = \varepsilon(k)\bar{\phi}_R(k + G). \tag{14}$$

We are free to pick the Fourier components of ϕ_R at all of the M k points within the first Brillouin zone (this freedom corresponds to the choice of the $C(k)$ function in equation (2)), but once this has been done the Fourier components throughout the rest of reciprocal space are determined by equation (14). Some sets of first-Brillouin-zone Fourier components will lead to localized basis functions and some will not, and the task facing us now is to decide on a useful and convenient choice. A direct attack on the problem is difficult, but the chemical pseudopotential method suggests an elegant indirect approach.

3. The chemical pseudopotential method

The above discussion applies to any set of basis functions spanning a band of eigenstates as long as all the basis functions look the same and there is one per unit cell. Now we want to concentrate on one particular set, the set of non-orthonormal chemical pseudopotential basis functions. To see how these are defined, let us go back and look at the closure relation (equation (3))

$$\hat{H}|\phi_R\rangle - \sum_{R'(\neq R)} D_{R',R}|\phi_{R'}\rangle = D_{R,R}|\phi_R\rangle. \tag{15}$$

This equation holds for any set of functions spanning the band and so we need to do more to specify the basis functions uniquely. There are several (related) ways forward, which are well summarized by Weeks *et al* [11], but Anderson's is probably the simplest. He defines the basis set by imposing an additional 'self-consistency' condition,

$$D_{R',R} = \langle \phi_{R'}|\hat{V}_{R'}|\phi_R\rangle \qquad (R \neq R') \tag{16}$$

where it has been assumed that the crystal potential $V(r)$ can be written as a sum of contributions from each unit cell

$$V(r) = \sum_R V_R(r). \tag{17}$$

Substituting the self-consistency condition into equation (15), one obtains

$$\left[\hat{T} + \hat{V}_R + \sum_{R'(\neq R)} \left(1 - |\phi_{R'}\rangle\langle\phi_{R'}| \right) \hat{V}_{R'} \right] |\phi_R\rangle = D_{R,R} |\phi_R\rangle \tag{18}$$

which is known as the chemical pseudopotential equation. Note that any potential can be decomposed into contributions from individual cells and so equation (18) can be exact. In practice, however, it is usually assumed that the cell potentials have some simple form (a screened atomic potential, for example, if there is just one atom per unit cell) and so an approximation is made at this stage.

Near lattice point R, the Hamiltonian in equation (18) looks rather like an atomic Hamiltonian (assuming, for simplicity, that there is just one atom per unit cell and that $\hat{V}_R$ is close to an atomic potential), but on other sites only weak 'chemical pseudopotentials' act

$$\hat{V}_{R'}^{cp} = \left(1 - |\phi_{R'}\rangle\langle\phi_{R'}| \right) \hat{V}_{R'}. \tag{19}$$

The removal of the projection along $|\phi_{R'}\rangle$ weakens the effective potential and so it is reasonable to hope that the chemical pseudopotential equation has localized atomic like solutions. These could be found by starting with a good guess (atomic orbitals, for example); constructing the corresponding chemical pseudopotentials; solving equation (18) once to find the output basis functions; using these to construct the new chemical pseudopotentials; and iterating until self-consistency is attained and the input and output basis functions are the same. During these iterations the **D** matrix elements will settle down to their proper values and the bandstructure of the crystal can then be deduced from equation (7), or by solving either of the two equivalent secular equations

$$\det(\mathbf{D} - \varepsilon \mathbf{I}) = 0 \qquad \det(\mathbf{H} - \varepsilon \mathbf{S}) = 0 \tag{20}$$

in a non-crystalline solid.

Anderson [12] carried through an approximate version of this procedure for the π bands on a chain of carbon atoms and found that the cancellation of the potentials on other sites was effective and that the basis functions were therefore very close to atomic eigenfunctions. Hoshino *et al* [13, 14] found approximate solutions for H_2^+ and for some small molecules containing only C atoms. In no other cases has the chemical pseudopotential equation been solved, however, and it has never been solved accurately. Indeed, it is not even clear that localized solutions always exist, although the assumption that they do and that they look like atomic orbitals has been behind many electronic structure calculations [15]. All this deserves to be investigated more thoroughly, which is the purpose of this paper.

There is one more point to be discussed before going on. Equation (18) is non-linear and so the normalizations of the states used in constructing the chemical pseudopotentials must be specified. This is easiest to understand by thinking about the iterative method of solution described above. The initial chemical pseudopotentials are constructed and then held fixed while equation (18) is solved to find the output basis functions. Because the chemical pseudopotentials are fixed during the iteration, the differential equation becomes linear and the normalizations of the output basis functions are arbitrary. However, the normalizations do matter when we come to construct the input chemical pseudopotentials for the next iteration, since the bigger the normalization the greater the amount of $\hat{V}_{R'}$ 'subtracted off.' It is usually assumed that it is best to use basis functions of unit normalization, but it

turns out that this is not necessarily true for the Kronig–Penney model since the chemical pseudopotential equation may not have solutions unless larger normalizations are allowed.

There is another way of viewing the freedom to choose the normalization: solving the chemical pseudopotential equation with $\langle\phi_{R'}|\phi_{R'}\rangle = w_{R'}$ is equivalent to solving the alternative equation

$$\left[\hat{T} + \hat{V}_R + \sum_{R'(\neq R)}(1 - |\phi_{R'}\rangle w_{R'}\langle\phi_{R'}|)\hat{V}_{R'}\right]|\phi_R\rangle = D_{R,R}|\phi_R\rangle \qquad (21)$$

with $|\phi_{R'}\rangle$ normalized to unity. The factor $w_{R'}$ (independent of R' in a perfect crystal), which was introduced as a normalization constant, may therefore also be viewed as a scale factor in the pseudopotential. We will take the second point of view from now on, allowing a scale factor in the pseudoptotential but insisting that all the basis functions are normalized (a procedure first suggested by Hoshino *et al* [13]). The Anderson self-consistency condition, equation (16), becomes

$$D_{R',R} = w_{R'}\langle\phi_{R'}|\hat{V}_{R'}|\phi_R\rangle \qquad (R \neq R') \qquad (22)$$

but little else changes.

4. Application to the Kronig–Penney model

The one-dimensional Kronig–Penney model is so simple that the chemical pseudopotential equation can be solved almost entirely analytically. This allows us to ascertain when solutions exist and when they do not, and to examine the basis functions all the way from the tight-binding to the nearly free electron limits. The results, shown in the figures, are quite surprising.

The Schrödinger equation for the one-dimensional Kronig–Penney model is

$$\left(-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - P\sum_n\delta(x-n)\right)\psi(x) = \varepsilon\psi(x). \qquad (23)$$

Lengths are measured in units of the lattice parameter and there are attractive delta functions of strength P at each lattice point. The magnitudes of the reciprocal lattice vectors are all integer multiples of 2π.

We are looking for a set of localized basis functions, one centred in each unit cell and all identical to within lattice translations, exactly spanning the lowest band of the Kronig–Penney model. Since the basis functions are all equivalent we will consider only ϕ_0 (the basis function centred at the origin) from now on. All perfect sets of localized basis functions have Fourier components that satisfy the Schrödinger equation in reciprocal space (see equation (14) and the preceding discussion) and hence

$$\frac{1}{2}(k+G)^2\bar{\phi}_0(k+G) + \sum_{G'}\bar{V}(G')\bar{\phi}_0(k+G-G') = \varepsilon(k)\bar{\phi}_0(k+G). \qquad (24)$$

The Kronig–Penney bandstructure is easy to calculate [17] and so we can assume that $\varepsilon(k)$ is known. The delta function form of the potential implies that

$$\sum_{G'}\bar{V}(G')\bar{\phi}_0(k+G-G') = \int V(x)\phi_0(x)\exp[-\mathrm{i}(k+G)x]\mathrm{d}x = -P\sum_m\exp(-\mathrm{i}km)\phi_0(m)$$

$$(25)$$

and hence equation (24) becomes

$$\bar{\phi}_0(k+G) = \frac{-P\sum_m \phi_0(m)\exp(-ikm)}{\varepsilon(k) - \frac{1}{2}(k+G)^2}.$$

(26)

So far all this applies for any set of perfect localized basis functions. The chemical pseudopotential basis functions also satisfy the Anderson self-consistency condition (in our slightly generalized form)

$$D_{m0} = \langle \phi_m | w\hat{V}_m | \phi_0 \rangle = -Pw\phi_m^*(m)\phi_0(m) = -Pw\phi_0^*(0)\phi_0(m) \qquad (m \neq 0)$$

(27)

where the **D** matrix elements are related to the bandstructure via

$$D_{m0} = \frac{1}{M}\sum_k \varepsilon(k)\exp(ikm) \qquad \varepsilon(k) = \sum_m \exp(-ikm)D_{m0}$$

(28)

and so are also known. Substituting equation (27) into equation (26) now gives

$$\begin{aligned}
\bar{\phi}_0(k+G) &= \frac{1}{w\phi^*(0)}\left(\frac{-Pw\sum_m \phi_0(m)\phi_0^*(0)\exp(-ikm)}{\varepsilon(k) - \frac{1}{2}(k+G)^2}\right) \\
&= \frac{1}{w\phi_0^*(0)}\left(\frac{-Pw|\phi_0(0)|^2 + \sum_{m(\neq 0)} D_{m0}\exp(-ikm)}{\varepsilon(k) - \frac{1}{2}(k+G)^2}\right) \\
&= \frac{1}{w\phi_0^*(0)}\left(\frac{Pw|\phi_0(0)|^2 - \varepsilon(k) + D_{00}}{\frac{1}{2}(k+G)^2 - \varepsilon(k)}\right).
\end{aligned}$$

(29)

The only unknown on the right hand side of this equation is $\phi_0(0)$, which is fixed by the condition that $\phi_0(x)$ must be normalized.

To apply the normalization condition, we start by writing down an explicit expression for $\phi_0(x)$

$$\begin{aligned}
\phi_0(x) &= \frac{1}{M}\sum_{k,G}\bar{\phi}_0(k+G)\exp[i(k+G)x] \\
&= \frac{1}{M}\sum_{k,G}\frac{1}{w\phi_0^*(0)}\frac{Pw|\phi_0(0)|^2 - \varepsilon(k) + D_{00}}{\frac{1}{2}(k+G)^2 - \varepsilon(k)}\exp[i(k+G)x].
\end{aligned}$$

(30)

Now we set the integral of $|\phi_0(x)|^2$ over the whole system equal to unity to obtain

$$1 = \frac{1}{M}\sum_{k,G}\frac{1}{w^2|\phi_0(0)|^2}\left(\frac{Pw|\phi_0(0)|^2 - \varepsilon(k) + D_{00}}{\frac{1}{2}(k+G)^2 - \varepsilon(k)}\right)^2$$

(31)

which is a quadratic equation of the form

$$aq^2 + bq + c = 0$$

(32)

for $q = |\phi_0(0)|^2$. In practice a, b, and c are evaluated numerically using the known bandstructure and value of D_{00}; equation (32) then gives $|\phi_0(0)|^2$; and equation (30) determines $\phi_0(x)$. It should be noted that in the limit $M \to \infty$, the sum over k in the

Brillouin zone and over reciprocal lattice vectors G may be replaced by a single integral over all k, $\varepsilon(k)$ being considered as a periodic function in reciprocal space.

The parameters a and c are explicitly positive and so the two roots of equation (32), if real, have the same sign. Since negative roots are unacceptable there will either be two acceptable solutions or no acceptable solutions, a unique solution existing only when $b^2 = 4ac$. In the limit as $w \to 0$, when the w^2 term in b can be ignored, we can use the Schwarz inequality [22] to prove that $b^2 - 4ac \leqslant 0$ and so there are no real solutions. In the limit as $w \to \infty$, b is < 0 and $b^2 \gg 4ac$ and so there are two real positive solutions, both of which are acceptable. As w increases from zero we therefore switch from a region where there are no solutions to a region where there are two solutions, without the intervention of a finite region in which there is a unique solution. The lack of solutions as $w \to 0$ makes good physical sense since the cancellation of the potential on other sites becomes ineffective in that limit and the chemical pseudopotential equation turns back into the original Schrödinger equation, but the fact that the solutions always come in pairs is surprising. This particular form of non-uniqueness may be specific to the Kronig–Penney model, of course, and there may be unique solutions for other models; but we have shown that multiple solutions are possible and see no reason why they should not occur in other cases.

The complication of multiple solutions may be avoided if we specify the (real) value of $\phi_0(0)$ instead of insisting that the basis functions are normalized. Then equation (30) allows us to construct a unique solution for any positive value of w. For small values of w (when we know there are no normalized solutions) the basis functions generated will have very large norms and so correspond to normalized solutions for a much larger value of w, but solutions can always be found and are always unique. We will stay with normalized basis functions, however, since that is what most users of chemical pseudopotentials do and we want to investigate the method as it is used rather than a close relative.

Before going on to look at the results, there is one point that confused us and needs clearing up. Setting $x = 0$ in equation (30) gives

$$|\phi_0(0)|^2 \left(1 - \frac{P}{M} \sum_{k,G} \frac{1}{\frac{1}{2}(k+G)^2 - \varepsilon(k)} \right) = \frac{1}{wM} \sum_{k,G} \frac{D_{00} - \varepsilon(k)}{\frac{1}{2}(k+G)^2 - \varepsilon(k)} \tag{33}$$

which looks like a sort of self-consistency relation fixing the value of $|\phi_0(0)|^2$ once and for all. In fact, it can be shown that both sides of this equation are equal to zero independent of the value of $|\phi_0(0)|^2$ and so $|\phi_0(0)|^2$ escapes undefined.

5. Results

In the extreme tight-binding limit the Kronig–Penney bandstructure is almost flat and accurate wavefunctions can be obtained by taking linear combinations of atomic orbitals. We would therefore expect the chemical pseudopotential method to work well. With this in mind we will start by considering the case when $P = 5$. The overlap s of atomic orbitals

$$\phi_{\text{atomic}}(x) = \sqrt{P} e^{-P|x|} \tag{34}$$

on adjacent sites is then just 0.04.

The $P = 5$ Kronig–Penney bandstructure is compared to the free electron bandstructure in figure 1(a) and the closeness to the tight-binding limit is obvious. As was explained in
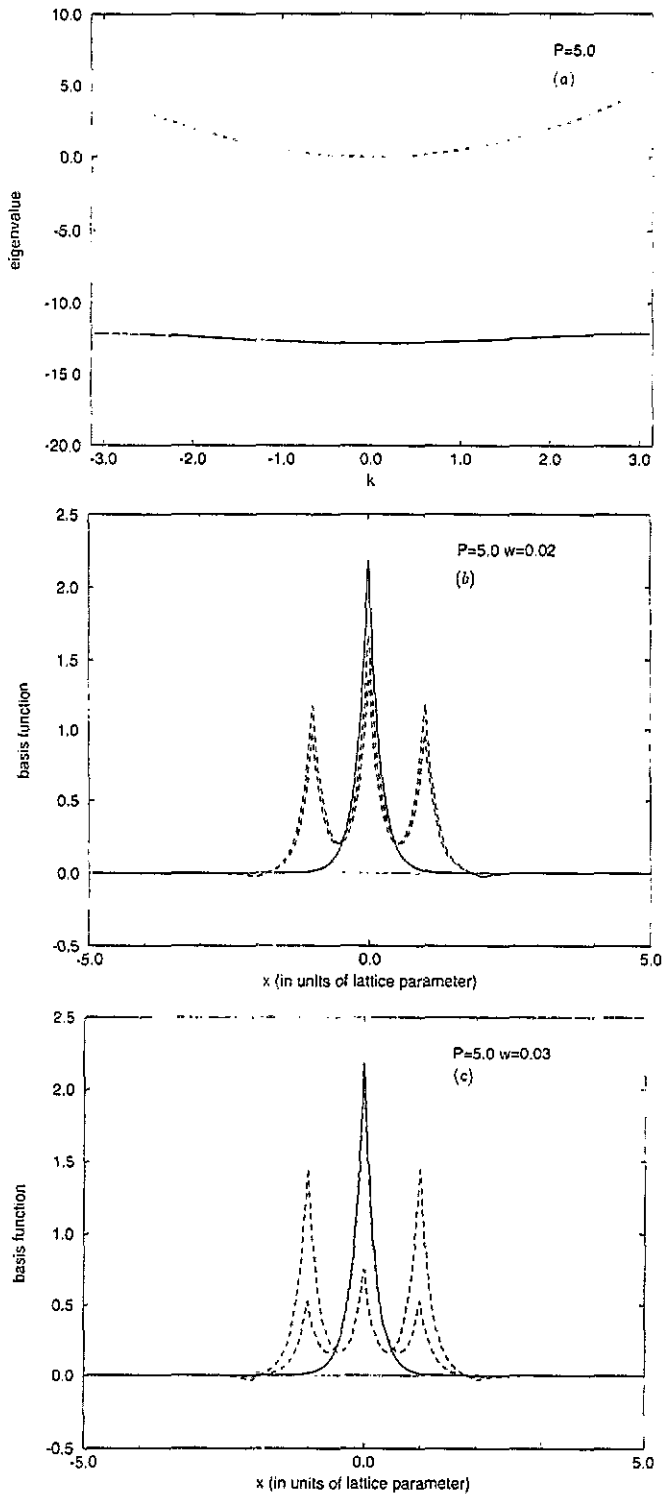
Figure 1. Results when $P = 5$: (a) bandstructures of the Kronig–Penney model (solid line) and free electrons (dashed line); (b)–(f) an atomic orbital (solid line) and the two solutions of the chemical pseudopotential equation for a variety of values of the w parameter.

Figure 1. (Continued)

Figure 2. Results when $P = 1$: (a) bandstructures of the Kronig–Penney model (solid line) and free electrons (dashed line); (b)–(f) an atomic orbital (solid line) and the two solutions of the chemical pseudpotential equation for a variety of values of the w parameter.
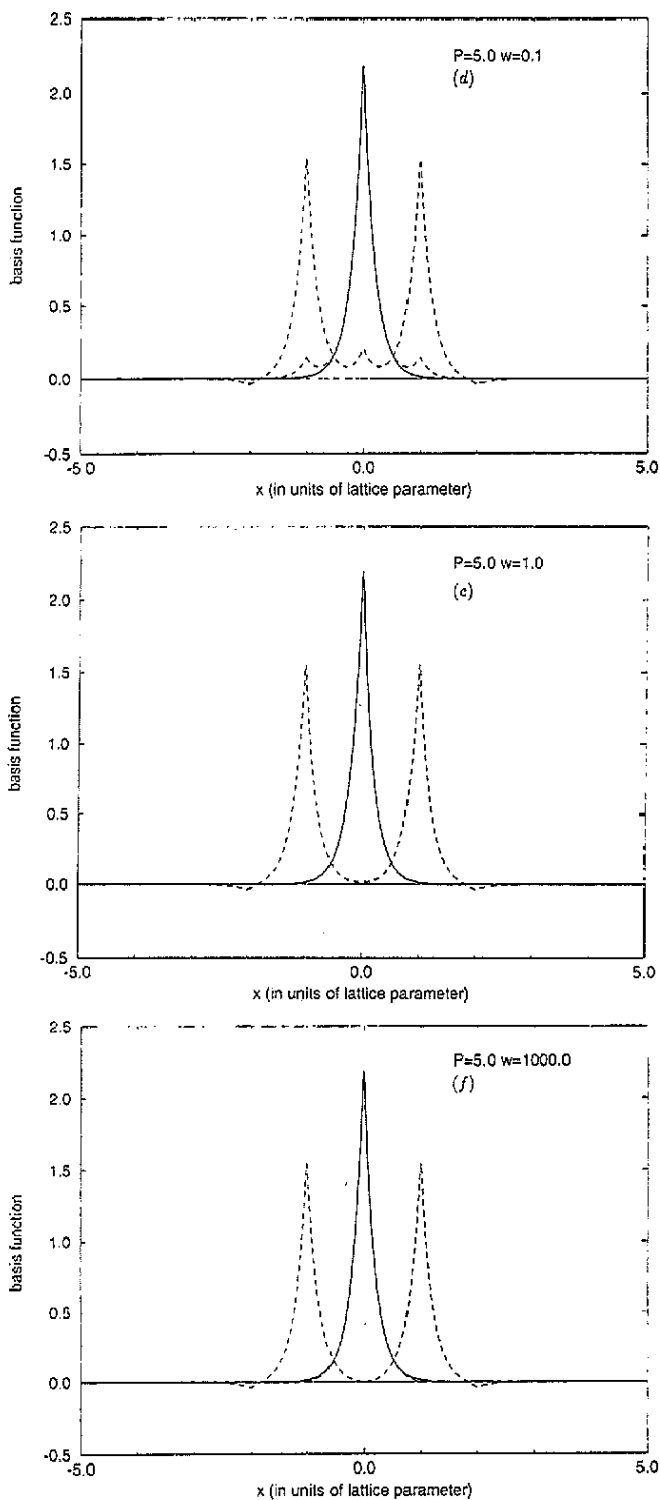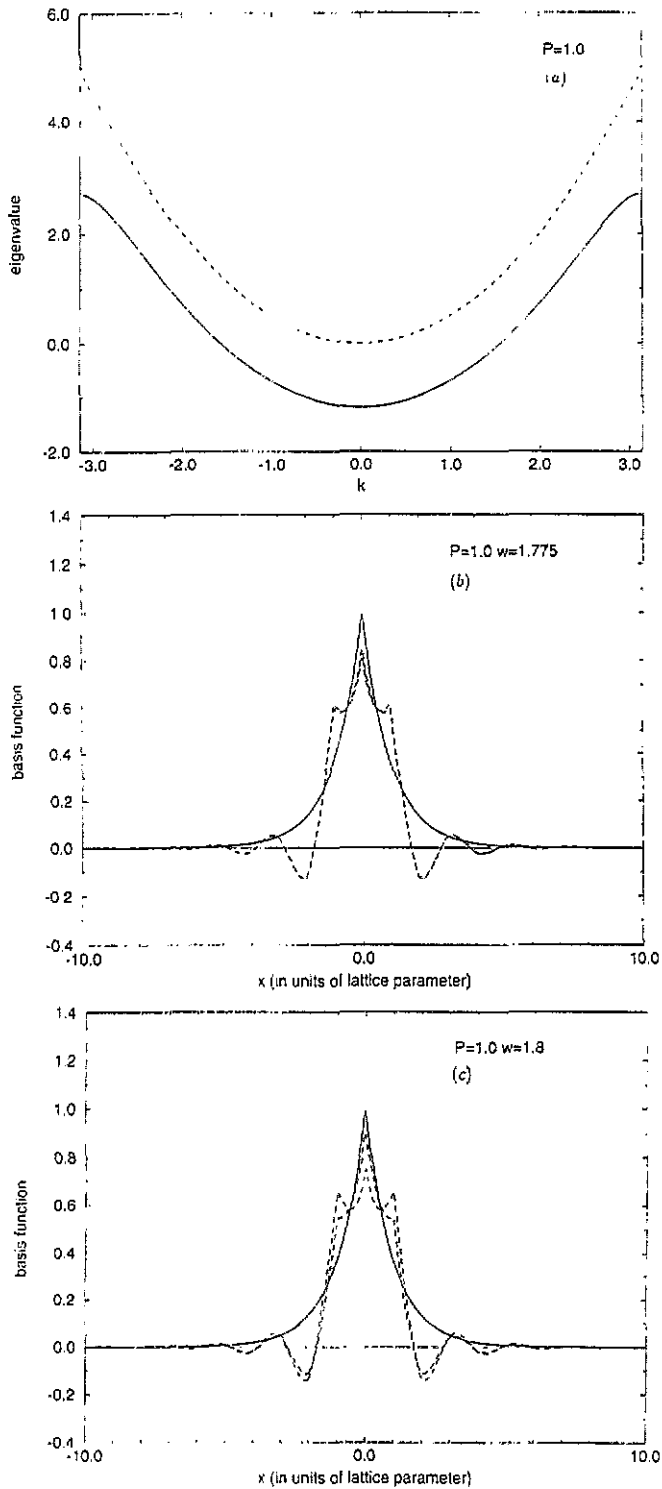
Figure 2. (Continued)

Figure 3. Results when $P = 0.1$: (a) bandstructures of the Kronig–Penney model (solid line) and free electrons (dashed line); (b)–(f) an atomic orbital (solid line) and the two solutions of the chemical pseudpotential equation for a variety of values of the w parameter.
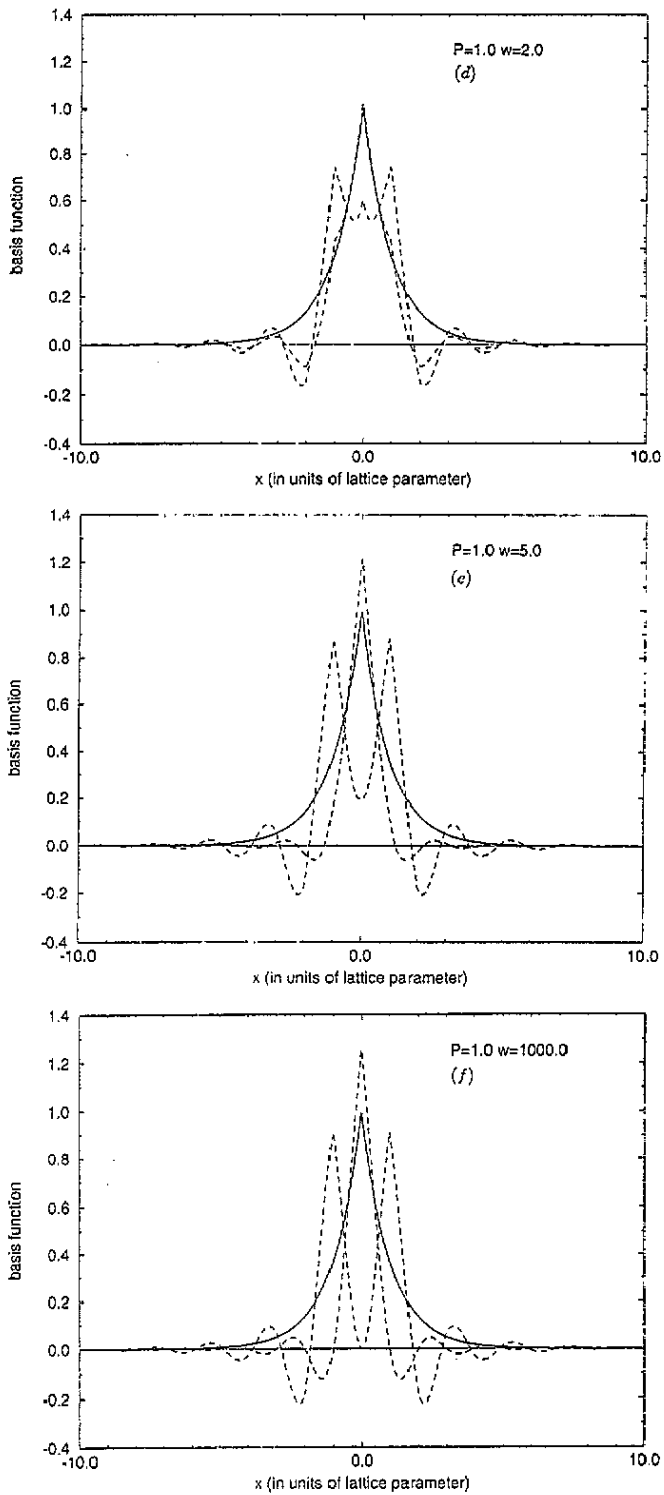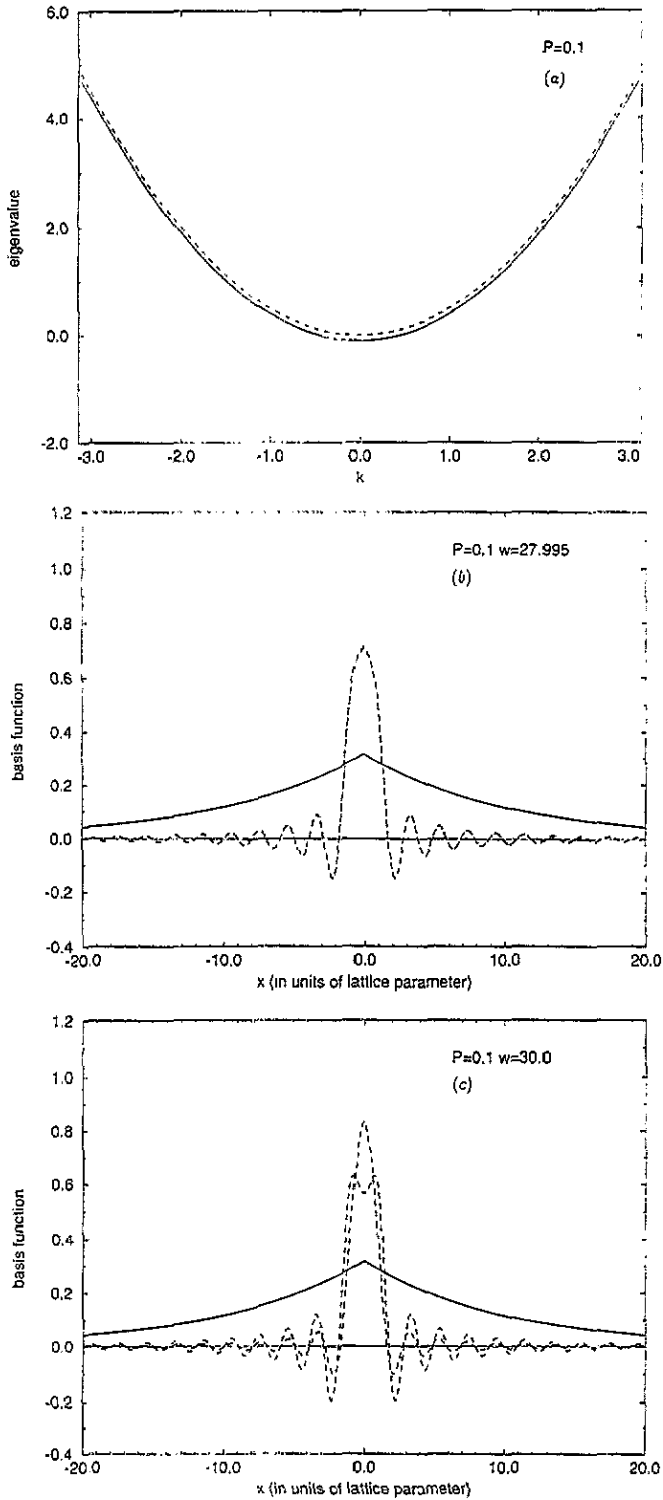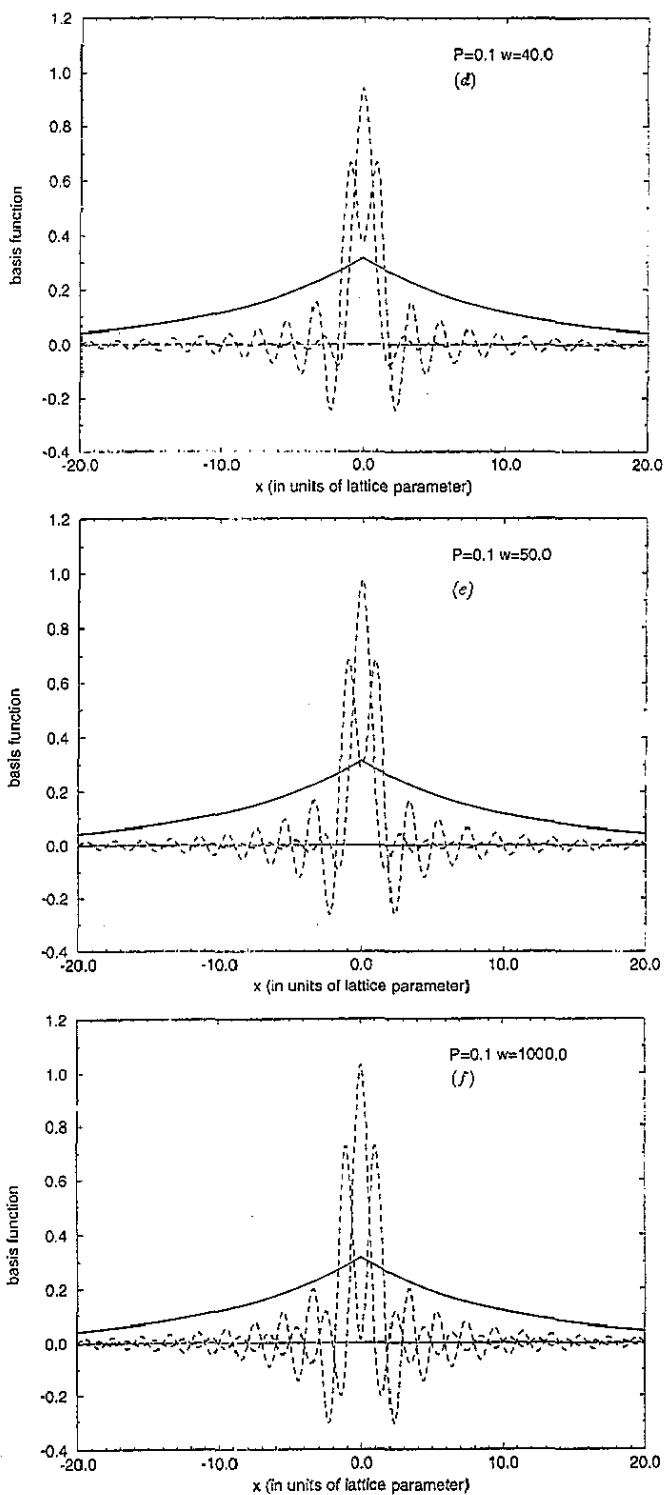
Figure 3. (Continued)

section 4, there is always a minimum value of w (called w_{min} from now on) below which the chemical pseudopotential equation cannot be solved. w_{min} decreases very rapidly as P increases and numerical experiments show that it lies somewhere between 0.015 and 0.020 when $P = 5$. This means that subtracting just one part in fifty of the projected potential on other sites is enough to localize the basis functions, which seems remarkable. The two solutions of the chemical pseudopotential equation are identical at w_{min} ($b^2 = 4ac$ in equation (32)) but soon begin to differ as w is increased. At $w = 0.02$, just above the minimum, they are as shown in figure 1(b) and are quite well localized. As w increases, the two solutions become more and more different (fFigure 1(c)–(e)), until in the very-large-w limit they are as shown in figure 1(f). One of the two solutions is the expected atomic function and has appreciable weight only on the atom at the origin, but the other is mostly on the two atoms either side of the origin and has almost zero weight on the central atom. One might expect that the most atomic-like solutions will occur when $w = 1$, since then the chemical pseudopotentials are substantially weakened by the subtraction of the projection along the basis function but the 'overshoot' that can happen at larger values of w is avoided. This expectation is supported by the results, although $w = 0.5$ (not shown) and $w \to \infty$ will do almost as well.

We have tested both solutions by checking that the appropriate Bloch linear combinations of the basis functions (cf. equation (1)) really do give the known eigenfunctions of the Kronig–Penney model. The tests were successful and so we are confident that the non-uniqueness is genuine. Note that both solutions correspond to exactly the same **D** matrix and so to the same (lowest) eigenvalue of the chemical pseudopotential equation—neither is an 'excited state.'

If we now decrease P (so increasing s), the value of w_{min} increases and reaches unity when $P \simeq 1.4018$ ($s \simeq 0.591$). For P values smaller than 1.4018, the usual version of the chemical pseudopotential equation (normalized basis functions with $w = 1$) cannot be solved, although solutions can still be obtained if larger values of w are allowed. As an example, let us now move on to the case when $P = 1$ and $s = 0.74$. The bandstructure, shown in figure 2(a), is somewhere between the tight-binding and nearly free electron limits. w_{min} lies between 1.770 and 1.775 and the basis functions for a selection of w values are shown in figure 2(b)–2(f). The best localized solution is found near $w = 5$ (the argument that one would expect the best localized solutions when $w = 1$ only works in the tight-binding limit—here the chemical pseudopotential equation cannot even be solved when $w = 1$) and is considerably more localized than an atomic orbital. Similar extra localization has been observed by Hoshino *et al* [13] in very different circumstances. Unfortunately, the short range of the basis functions does not imply a correspondingly short ranged **D** matrix, since the large value of w makes the off diagonal **D** matrix elements very sensitive to the small tails of the basis functions. This is an example of a point we have already discussed—that the degree of localization of the basis functions is irrelevant because the **D** matrix is fixed by the bandstructure.

For very small values of P, w_{min} becomes proportional to $1/P$ and increases rapidly. A bandstructure for $P = 0.1$, $s = 0.995$, is shown in figure 3(a) and is very close to a free electron bandstructure. The value of w_{min} is now between 27.990 and 27.995 and the two chemical pseudopotential basis functions for $w = 27.995$ are shown in figure 3(b) (this is so close to w_{min} that the two solutions are indistinguishable). They are very long ranged, extending over at least 20 atoms, but are still much more localized than atomic orbitals. One of the two basis functions shrinks noticeably as w grows, becoming optimally localized near $w = 40$, but then becomes less localized again as w carries on increasing.

6. Conclusions

Chemical pseudopotential theory has been around for a long time and is elegant and plausible. However, it was invented in the days when computing was difficult and was not tested properly as a result. An approximate version of chemical pseudopotentials has already been widely and successfully used by Bullett [15], but there is evidence [23] that the approximations involved do not work well for solid H, and some recent work by one of us [24] shows that they also fail for Ge. It is reasonable to hope that a less approximate implementation may become the basis of a quick and accurate $\mathcal{O}(N)$ bandstructure method, but this is not yet clear and will not become clear until we know more about chemical pseudopotentials in general. Does the chemical pseudopotential equation have solutions in real solids? Are those solutions unique if they do exist? How closely do the chemical pseudopotential basis functions resemble atomic orbitals? What is the best value of w? Is the numerical task of solving the chemical pseudopotential equation in a real solid so forbidding as to rule out the method in practice? All these questions will need answers if chemical pseudopotentials are ever to become an accurate bandstructure method and this paper represents a first attempt to address some of them.

In section 2 we discussed 'perfect' localized basis sets in general. We clarified the limited freedom available in choosing the basis functions and remarked on the fact that the **D** matrix is fixed by the bandstructure so that to some extent the degree of localization of the basis functions is irrelevant. Then we introduced the chemical pseudopotential method and explained how it can be solved almost analytically for the one-dimensional Kronig–Penney model. For this example, we showed that the usual version of the chemical pseudopotential equation, in which the basis functions are normalized to unity, has solutions only in the tight-binding limit. However, introducing the parameter w, which may be regarded as either an arbitrary basis function normalization or as a multiplying factor in the pseudopotential, allows solutions to be found in all cases. The main surprise was that the solutions are never unique, but always come in pairs. It is possible that this non-uniqueness is specific to the Kronig–Penney model and does not occur in real solids, but we are far from convinced that this is the case. In the nearly free electron limit we found that the chemical pseudopotential basis functions were much more localized than atomic orbitals even though the **D** matrix becomes rather long ranged (the matrix elements would decay as r^{-2} for free electrons). This makes clear the error in confusing the range of the **D** matrix (which is fixed by the bandstructure) with the range of the basis functions (which is not).

Fortunately, our results certainly do not rule out the idea of basing an accurate bandstructure method on chemical pseudopotential theory. It seems likely that reasonably localized basis functions do exist in most solids and that they can be calculated by solving the local chemical pseudopotential equation. The probable lack of uniqueness in the solutions may be an annoyance but is unlikely to be anything worse than that, and so the possibility remains that chemical pseudopotentials may lead to a local bandstructure method with no basis set errors.

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