k-point sampling and the k.p method in pseudopotential total energy calculations

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I J Robertson and M C Payne

Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

Abstract. A fast method is presented for the calculation of total energies within the density functional formalism for systems that require a large number of *k*-points. Approximate solutions at a large number of *k*-points are obtained from exact self-consistent solutions at a smaller number of *k*-points using an extension of the *k · p* method. The method is demonstrated by a calculation of the total energy of FCC aluminium at a series of lattice parameters. An analysis is presented that partitions the errors in the calculations into those inherent in any finite sampling procedure and those that are specific to the *k · p* method. The extra error due to the *k · p* method is shown to be around 10% of energy differences for these calculations but a simple modification to the calculations requiring no more computational time reduces this error to 2%. For these simple calculations the time saved by using the *k · p* method is fairly small but for larger calculations the method is several orders of magnitude quicker. Errors from either source are shown to be far less important in the electronic potentials than in the eigenvalue sums. It is concluded that in any total energy calculation fewer *k*-points are required to describe the potential than to calculate the eigenvalue sum. This could be exploited to gain an order of magnitude saving in computational time in any calculation.

1. Introduction

The exact calculation of the total energy of an infinite structure is an intractable problem. A considerable number of simplifications and approximations are required to reduce the problem to one that can be addressed computationally. Density functional theory provides a method for dealing with the electron–electron interaction by mapping the system of interacting electrons to a system of non-interacting electrons. The system of non-interacting electrons is described by the solutions of the Kohn–Sham equations (Kohn and Sham 1965): these are single particle equations which must be solved self-consistently. In principle a calculation for an infinite bulk solid would require that the Kohn–Sham equations are solved to determine the wavefunctions of an infinite number of electrons. Obviously the problem remains intractable in this form. Some method is required for approximately representing this infinite number of electrons by a finite number of electrons. In the case of a periodic system this is achieved by applying Bloch's theorem (see Ashcroft and Mermin 1976). By suitable choice of supercell even aperiodic structures such as surfaces can be considered to be periodic so that Bloch's theorem may be applied.

Bloch's theorem states that in periodic system the wavefunctions of the electrons can be written as follows

$$\Psi_{kn} = U_{kn} \exp(i\mathbf{k} \cdot \mathbf{r})$$

where $U_{kn}(\mathbf{r})$ has the periodicity of the system. $\mathbf{k}$ is the k-point label which conventionally takes all values in the first Brillouin zone. The solution of the Kohn–Sham equations at a single k-point is computationally tractable. Therefore the electronic eigenstates and their corresponding eigenvalues can be calculated at any k-point. All the eigenstates whose energies lie below the Fermi energy are occupied. The total energy of the system depends on the eigenvalues and charge densities generated by all of the occupied states so that in principle, calculations have to be performed at an infinite number of k-points. In practice some method must be applied to reduce this to a finite number of calculations.

The k-points lie within a finite volume of reciprocal space. However, the properties of two wavefunctions on a given band with similar values of $\mathbf{k}$ are expected to be very similar. If this is the case the electronic states in a region of $\mathbf{k}$ space may be accurately represented by the state at the centre of the region. Thus the infinite number of k-points can be replaced by a finite number of k-points lying within the first Brillouin zone.

In the past methods have been developed to optimize the choice of k-points for completely filled bands so that the charge density and total energy can be accurately calculated using a very small number of so called 'special k-points' (Baldereschi 1973, Chadi and Cohen 1973, Monkhorst and Pack 1976). In these methods symmetry arguments are employed to deduce those k-points which are expected to be particularly representative of the properties of the whole Brillouin zone. Although the absolute energies calculated with small k-point sets are expected to be poor, when calculating the energy differences between similar structures the errors will tend to cancel so that the errors in the energy differences will be much smaller (Cheng *et al* 1987). Nevertheless when comparing dissimilar structures the k-point sampling errors from different k-point sets are unlikely to cancel and so a much larger number of k-points will be required to compute energy differences.

Problems also arise in the case of metals because some the bands are only partially occupied. The problem of sampling k-space is particularly acute around the Fermi surface because of discontinuities in functions such as

$$\rho_k(\mathbf{r}_0)$$

where ρ is the charge density, as $\mathbf{k}$ crosses the Fermi surface. Such discontinuities require extremely large numbers of k-points for accurate calculation of charge densities and total energies.

The two problems outlined above point to the need for large numbers of k-points in many calculations. However, the computational time scales linearly with the number of k-points used in the calculation, so that absolute k-point convergence can often not be achieved in realistic amounts of computational time. What is required is a quicker method of obtaining data from large numbers of k-points which albeit less accurate than traditional methods is still accurate enough to be useful.

One method for generating information at additional k-points is the $\mathbf{k} \cdot \mathbf{p}$ method (see Harrison 1970). In the past the $\mathbf{k} \cdot \mathbf{p}$ method has been used as a cheap method of obtaining non-self-consistent band structures. In this paper we investigate the possibility of extending the $\mathbf{k} \cdot \mathbf{p}$ method to perform cheap fully self-consistent total energy calculations with a large number of k-points. In the following sections we will introduce

and explain the total energy $k \cdot p$ method and investigate the errors associated with the method by performing calculations for FCC aluminium.

In section 2, the $k \cdot p$ method is outlined and its performance in predicting eigenvalues is reviewed and extensions that are required to allow the $k \cdot p$ method to be used for total energy calculations are described. In section 3 the computational method for implementing a $k \cdot p$ scheme is briefly described. Section 4 outlines the use of the Harris energy functional (Harris 1985) in conjunction with the $k \cdot p$ method. The Harris energy functional facilitates an analysis of the errors unique to the $k \cdot p$ method and those inherent in any finite sampling technique. Section 5 analyses these two sources of error and assesses their relative magnitudes in the case of absolute energies and energy differences. The calculations we have performed to analyse the errors are a severe test of the $k \cdot p$ method since we attempt to obtain the electronic states over a large Brillouin zone from the solutions at a single k-point positioned at the edge of the irreducible zone. The errors will be reduced at no computational cost by using any other sampling point. It is also possible to make the errors arbitrarily small by using a larger number of k-points or a larger number of electronic bands, although this incurs a computational cost. Section 6 discusses the computational time required by the $k \cdot p$ method. Finally section 7 presents the conclusions of our analysis and lists some of the directions that future work may take.

2. The $k \cdot p$ method

2.1. $k \cdot p$ eigenvalues

Consider the Kohn–Sham equation for some periodic potential $V(r)$:

$$[(\hbar^2/2m)\nabla^2 + V(r)]\Psi_{kn} = E_{kn}\psi_{kn}. \tag{1}$$

Where $V(r)$ is the sum of the Hartree, exchange–correlation and ionic potentials, E_{kn} is the eigenvalue of the nth band at k-point k and ψ_{kn} is the wavefunction of the nth band at k. Since $\Psi_{kn} = U_{kn} \exp(ik \cdot r)$ we can substitute back into (1) to give

$$[-(\hbar^2/2m)\nabla^2 + V(r) + k^2 + 2k \cdot p]U_{kn}(r) = E_{kn}U_{kn}(r) \tag{2}$$

where p is the quantum mechanical operator. For $k = 0$ we have

$$[-(\hbar^2/2m)\nabla^2 + V(r)]U_{0n}(r) = E_{0n}U_{0n}(r). \tag{3}$$

If we use a basis of N plane waves then there are N independent solutions to (3). Suppose that we write the solution at some other k-point k as a superposition of the lowest N_0 of the solutions at the point $k = 0$ so that

$$U_{kn}(r) = \sum_{i=1}^{N_0} a_{ik} U_{0i}(r). \tag{4}$$

Inserting (4) into (2) gives

$$\sum_{i=1}^{N_0} a_{ik}(E_{0i} + k^2 + 2k \cdot p)U_{0i}(r) = E_{kn} \sum_{i=1}^{N_0} a_{ik} U_{0i}(r). \tag{5}$$

Premultiplying both sides by U_{0j}^* and integrating over all space gives

$$\sum_{i=1}^{N_0} a_{ik}[(E_{0i} + k^2)\delta_{ji} + \langle j|2k \cdot p|i\rangle] = E_{kn}a_{jk}. \tag{6}$$

In the limit when the number of plane waves, N, and the number of solutions at $k = 0$,

Table 1. Twice the sum of six lowest eigenvalues at various points (k) within Brillouin zone (k) for FCC aluminium with lattice parameter of 4.15 Å: (a) using cut-off energy of 100 eV ($\Sigma\text{eig}_{100\,\text{eV}}$); ($b$) using $k \cdot p$ method with 19 bands ($\Sigma\text{eig}_{k \cdot p}$); ($c$) using cut-off energy of 20 eV ($\Sigma\text{eig}_{20\,\text{eV}}$). The electronic potential is the self-consistent potential produced by the occupied states at $k = 0$.

k (π/a)	$\Sigma\text{eig}_{100\,\text{eV}}$ (eV)	$\Sigma\text{eig}_{k \cdot p}$ (eV)	$\Sigma\text{eig}_{20\,\text{eV}}$ (eV)
0, 0, 0	−29.489	−29.489	−24.240
0, 0, 0.5	−30.940	−30.841	−25.025
0, 0.5, 0.5	−33.014	−32.810	−27.730
0.5, 0.5, 0.5	−35.194	−34.904	−30.435
0, 0, 1	−23.201	−23.014	−20.235
0, 0.5, 1	−32.393	−32.026	−28.480
0.5, 0.5, 1	−41.535	−40.981	−36.726
0, 1, 1	−30.201	−29.594	−26.182
0.5, 1, 1	−39.385	−38.512	−34.554
1, 1, 1	−37.690	−36.181	−32.276

N_0, are equal (6) would yield the exact solutions in the space defined by the N plane waves. Reducing the value of N_0 introduces an error into the solutions whose magnitude will be related to the contribution to a given U_{kn} from the U_{0m} removed from the basis set. It is expected that the magnitudes of these contributions would diminish as the difference between the energies E_{kn} and E_{0m} increases. The essence of the $k \cdot p$ method is to solve for the low energy eigenstates at arbitrary k-points using significantly less than N of the low energy eigenstates at $k = 0$, thus speeding up the process of calculating eigenstates away from $k = 0$ but without sacrificing too much of the accuracy. It should be noted that the choice of $k = 0$ as the k-point about which one performs $k \cdot p$ is certainly not unique. One may use any point or indeed any set of points.

The potential gain in speed of the $k \cdot p$ method is obvious. For instance, suppose that we choose to solve (6) by matrix diagonalization. Since the time taken to diagonalize a matrix goes up as the cube of the dimension of the matrix, use of the truncated basis N_0 is expected to increase the speed by a factor of $(N/N_0)^3$ over the solution of the N-dimensional problem. The computational times for other methods of solving (6) scale differently and detailed analysis of the time saving will be left to a later section.

The price that one must pay for this gain in speed is a corresponding loss of accuracy. Consider first the error in calculating eigenvalues for a fixed potential. Table 1 shows twice the sum of the six lowest eigenvalues calculated with a fixed potential for various points in the Brillouin zone. These have been calculated in three different ways: firstly with the $k \cdot p$ method using 19 bands; secondly with a full matrix diagonalization using a cut-off energy for the plane wave basis set of 100 eV; thirdly with diagonalization and a cut-off energy of 20 eV which gives a basis set of 19 plane waves. As expected, the $k \cdot p$ error increases with increasing extrapolation distance and is necessarily positive. In any particular direction the variation of the error is roughly quadratic, although the error is not isotropic. The errors for the calculation with the 20 eV cut-off energy are much larger than the $k \cdot p$ errors. The results show that the 19 bands at $k = 0$ form a much better basis set than 19 plane waves.

Closer to the point $k = 0$, the errors in the $k \cdot p$ calculation become both isotropic and quadratic. We have calculated the eigenvalue sums using both the $k \cdot p$ method and

Table 2. Twice the sum of six lowest eigenvalues at various points (**k**) close to **k** = 0 for FCC aluminium with lattice parameter of 4.15 Å: (*a*) using cut-off energy of 100 eV (Σeig$_{100\text{eV}}$); (*b*) Using **k** · **p** method with 19 bands (Σeig$_{k\cdot p}$). The electronic potential in each case is the self-consistent potential produced by the occupied states at **k** = 0.

k (π/a)	$\|\boldsymbol{k}\|$ (π/a)	Σeig$_{100\text{eV}}$ (eV)	Σeig$_{k\cdot p}$ (eV)	Σeig$_{k\cdot p}$ − Σeig$_{100\text{eV}}$ (eV × 10^{-4})
0, 0, 0	0.0	−29.48946	−29.48946	0
0, 0, 0.05	0.05	−29.80329	−29.80234	9.5
0, 0.05, 0.05	0.071	−29.73923	−29.73730	19.3
0.05, 0.05, 0.05	0.087	−29.67518	−29.67230	28.8
0, 0, 0.1	0.1	−30.33621	−30.33231	39.0
0, 0.05, 0.1	0.112	−30.27221	−30.26734	48.7
0.05, 0.05, 0.1	0.122	−30.20822	−30.20232	59
0, 0.1, 0.1	0.141	−30.08023	−30.07232	79.1
0.05, 0.1, 0.1	0.15	−30.01627	−30.00738	88.9
0.1, 0.1, 0.1	0.173	−29.82440	−29.81224	120

full diagonalization for a set of points which are 10 times nearer to the origin than those displayed in table 1. These results are shown in table 2. The isotropic and quadratic behaviour is clearly displayed in this table. The error in the **k** · **p** calculation is equal to $0.4k^2$ where **k** is measured in units of π/a, *a* is the lattice constant of FCC aluminium and the error is measured in eV.

2.2. Extension to total energy calculations

The sum of the eigenvalues is just one component of the total energy. Furthermore, the eigenvalues should be calculated using the self-consistent charge density. In this section we describe how one can calculate the other components of the total energy from **k** · **p** theory and the charge density, which allows one to iterate to self-consistency.

2.2.1. Charge density. The charge density is easy enough to express in terms of the **k** · **p** solutions

$$\rho(\boldsymbol{r}) = \sum_{k,n} w_{kn} U_{kn}^*(\boldsymbol{r}) U_{kn}(\boldsymbol{r}) \tag{7}$$

where the w_{kn} are the occupation probabilities of the various solutions which are determined by a Fermi function. *k* and *n* are summed over the values for which one has **k** · **p** solutions.

However, (7) is not useful in practice since explicit evaluation of all the U_{kn} would be computationally expensive. Instead one wishes to express the charge density in terms of the known solutions at **k** = 0.

Since we know that

$$U_{kn}(r) = \sum_m^{N_0} a_{knm} U_{0m}(r) \tag{8}$$

we may substitute (8) back into (7) to obtain

$$\rho(r) = \sum_{k,n} w_{kn} \sum_m^{N_0} \sum_{m'}^{N_0} a_{knm}^* a_{knm'} U_{0m}^*(r) U_{0m'}(r). \tag{9}$$

Reversal of the order of summation yields

$$\rho(r) = \sum_m^{N_0} \sum_{m'}^{N_0} \left(\sum_{k,n} w_{kn} a_{knm}^* a_{knm'} \right) U_{0m}^*(r) U_{0m'}(r). \tag{10}$$

The quantity in large brackets is an N_0-by-N_0 matrix which is easily obtained as a by-product of the process with which one finds the $k \cdot p$ eigenvalues. As such its extra computation time is negligible. After solution at all k points, one must sum over m and m' at each point in real space to obtain the charge density. The computational time for this process is independent of the number of k points and is proportional to $N_r N_0^2$, where N_r is the number of real space grid points in the unit cell. For large numbers of k points, this ensures that computing the charge density will not be a critical process so that the calculation of the charge density will take no longer than the determination of the eigenvalues.

2.2.2. Total energies. The total energy consists of a number of components. Two of them, the Ewald energy and the pseudopotential core energy are functions of only the ion types, positions and unit cell parameters. They are independent of the electronic structure and hence the k-point sampling. Other components of the total energy, the Hartree energy, the electron-ion energy and the exchange–correlation energy are functions of the charge density. As such they are straightforward to evaluate once the charge density has been calculated. Eigenvalues are obtained directly from the $k \cdot p$ process and may be summed with appropriate weightings.

2.2.3. Forces. For many applications one requires knowledge of the forces on the atoms and stresses on the unit cell. Some components of these quantities are independent of the electronic structure, some are functions of the charge density and one depends on the kinetic energy of each solution. Using the techniques outlined above all of these quantities can be calculated without explicit evaluation of the U_{kn}. Thus the calculation of forces and stresses is no more time consuming than evaluation of the eigenvalues.

It is clear then that the terms required for the extension of the $k \cdot p$ method to total energy calculations are readily computed and for large k-point sets these will not significantly increase computation times. What is not clear, is the extent to which the errors in the eigenfunctions, eigenvalues, charge densities and potentials lead to errors in the calculation of total energy and total energy differences. This question is addressed in section 5.

3. Structure of a $k \cdot p$ total energy calculation

A $k \cdot p$ total energy calculation can be thought of as executing in two distinct stages. In the first stage one must generate N_0 solutions at the point k_0 from which one intends to

perform **k** · **p** calculations. These solutions have been obtained by relaxation to near self-consistency by a Car–Parinnello (1985) scheme as modified by Payne *et al* (1986) with the ionic positions kept frozen. In this work, the point k_0 has been chosen to be the point $k = 0$. Again it should be stressed that there is no reason why one should not choose an alternative k-point or indeed a mesh of k-points.

In the second stage of the calculation, one uses the N_0 states at $k_0 = 0$ as a basis to derive the **k** · **p** solutions over a Monkhorst–Pack grid of other k points. A new estimate for the charge density and hence the potential is calculated from the occupied eigenstates of the grid. In the present work the occupancy of a state is calculated using the technique developed by Fu and Ho (1983) with an energy broadening of 0.04 eV. The $k = 0$ solutions are then allowed to evolve under the updated Hamiltonian and the whole procedure iterated to as near self-consistency as required.

4. The Harris energy functional

As stated in the previous section, one can iterate the many k-point calculation to as near charge self-consistency as required. The computational time taken is proportional to the number of iterations. To make this time as small as possible, we want to evaluate the energy at each iteration using an energy functional which is stationary at the ground state density so that the errors in the energy will be second order with respect to the errors in the charge density. One energy functional that fulfils this criterion is the Harris energy functional which is defined as:

$$H = \sum_i \varepsilon_i w_i - E_H[n_{in}(r)] + E_{XC}[n_{in}(r)] - \int d^3r \, \mu_{XC}[n_{in}(r)]n_{in}(r) + E_{nn} \qquad (11)$$

where E_H is the Hartree energy, E_{XC} is the exchange–correlation energy, E_{nn} is the nuclear–nuclear interaction, μ_{XC} is the exchange correlation potential, ε_i is the ith eigenvalue and w_i is the corresponding occupation probability. This expression is made up of terms which are functions of the input charge density and a term which is the weighted sum of the output eigenvalues. The output charge density *does not* appear in the expression. An alternative choice for the energy functional would be the Kohn–Sham functional. We prefer the Harris functional over the Kohn–Sham functional because it does not require knowledge of the output charge density or of the output kinetic energy. Neither of these quantities are particularly computationally expensive to evaluate, but not having to calculate them does provide a small saving in time.

Having used a stationary expression for the energy so that the number of iterations required will be as small as possible, the question remains, how many iterations are required? The answer to this question will vary from structure to structure and depends on the difference between the potential produced by the single k-point and that produced by the large number of k-points. For any given situation the best that one may hope for is that no additional iterations toward self-consistency are required. That is to say that it is possible to use only the self-consistent potential of the occupied states at $k = 0$ when computing the **k** · **p** total energy.

This use of no additional self-consistency iterations is not as crude as may first be thought. In the idealized case of a free electron meal all states produce the same charge density. For a nearly free electron metal such as aluminium, one might reasonably expect that the charge produced by different **k** points would be very similar. Consequently, it seems likely that the charge density and potential produced by the $k = 0$ states would be

Table 3. Variation with respect to grid size of the eigenvalue sum (Σeig) and Harris fuinctional (E_{Harris}) after no $k \cdot p$ iterations for FCC aluminium with a lattice parameter of 4.15 Å.

Grid	Σeig (eV)	E_{Harris} (eV)
2^3	-34.90352	-230.27300
4^3	-35.12805	-230.50908
6^3	-35.49425	-230.87690
8^3	-35.49636	-230.87205
10^3	-35.45114	-230.82578
12^3	-35.42582	-230.80069
14^3	-35.42844	-230.80447
16^3	-35.43638	-230.81387

close to the true self-consistent charge density and potential generated by many k points. The effect of any discrepancies that do exist will to a certain extent be reduced by use of the Harris functional, which near the ground state density shows errors in the energy which are second order in the error in charge density. All of this would seem to suggest that use of the Harris functional with no self-consistency iterations may be an adequate and straightforward method of energy evaluation for the second part of the $k \cdot p$ total energy calculation.

To test the validity of this scheme, we consider a single fixed structure, FCC aluminium with a lattice parameter of 4.15 Å. We calculate the total energy for Monkhorst–Pack grids of $2 \times 2 \times 2$, $4 \times 4 \times 4$, $6 \times 6 \times 6$, $8 \times 8 \times 8$, $10 \times 10 \times 10$, $12 \times 12 \times 12$, $14 \times 14 \times 14$, $16 \times 16 \times 16$ using up to 20 iterations. From now on we will refer to such grids as 2^3, 4^3 etc. A unit cell of four atoms is used and a plane wave basis set with a cut-off energy of 100 eV. The pseudopotential is that of Goodwin *et al* (1990) and we use the exchange and correlation function of Ceperley and Alder (1980) as parametrized by Perdew and Zunger (1981). The value of the Kohn–Sham functional after 20 self-consistency iterations and the Harris expression before any self-consistency iterations are shown in tables 4 and 3 respectively.

Comparison of the results shown in tables 3 and 4 show that the use of the Harris functional with the charge derived from only the $k = 0$ states introduces an error in the total energy of only 3×10^{-3} eV. (Note that the eigenvalue sum on the first and 20th self-consistency iteration differ by 0.08 eV. That is more than an order of magnitude greater than the error in the total energy.) For other sizes of unit cell the magnitude of the error in the total energy is comparable and the sign is always the same. Consequently one would expect that this error would be even less for energy differences.

In this work, we will be looking at energy differences of the order of 0.1 eV. It is clear that in this context, the error introduced by use of the Harris functional with no self-consistency iterations is insignificant. From now on all energies will be evaluated using this scheme.

The idea of using a different numbers of k-points to represent the potential and to evaluate the eigenvalue sum can be incorporated in any computational method. In the present case the potential is adequately represented by the potential produced by only the $k = 0$ states. In general this will not be the case, although the stationary property of the Harris functional will ensure that one may always realistically use fewer states in representing the input charge density than in representing the output eigenvalue sum.

Table 4. Variation with respect to grid dimension of the eigenvalue sum (Σeig) and Kohn–Sham energy functional (E_{tot}) after 20 $k \cdot p$ iterations for FCC aluminium with lattice parameter of 4.15 Å.

Grid	Σeig (eV)	E_{tot} (eV)
2^3	−34.82323	−230.27592
4^3	−35.05899	−230.51167
6^3	−35.42590	−230.87859
8^3	−35.42140	−230.87408
10^3	−35.37541	−230.82810
12^3	−35.34996	−230.80264
14^3	−35.35379	−230.80647
16^3	−35.36305	−230.81574

Structures which require self-consistency iterations in the second stage of the program do not invalidate the $k \cdot p$ method since the self-consistency iterations can be performed cheaply using the method outlined in section 2.

For the purposes of this paper there is another advantage of the Harris functional in that it allows an easy analysis of the errors due to the $k \cdot p$ method and those due to any finite sampling procedure. This is because the only variable quantity in the Harris expression for total energy after no self-consistency iterations is the eigenvalue sum, although even this is a function of that fixed input potential produced by the states at $k = 0$. The difficult problem of analysing the behaviour of the self-consistent total energy with respect to sampling procedure is thus reduced to a much easier problem. That is the problem of the variation in the sum of eigenvalues of a fixed single-particle Hamiltonian with respect to different grids and with respect to different methods of solution. In considering the total energy, it is no longer necessary to consider anything but the eigenvalue sum, and it is no longer necessary to worry about how the self-consistent potential varies as more k-points are added. With the help of this considerable simplification we turn to an analysis of the errors expected for a fixed structure and the errors in energy differences.

5. Errors in total energy calculations

5.1. General considerations

In the previous section we explained that in analysing the total energy of a fixed structure with respect to sampling procedure, it is possible to remove all but the contribution of the eigenvalue sum. In this section we use this fact to investigate the errors in calculating the total energy of a fixed structure and the errors in calculating energy differences between different structures. We also attempt to partition the error into that part which is due to the approximate nature of the $k \cdot p$ method and that part which is due to the approximation inherent in describing an infinite number of k points with a finite number of k points. The former will be called the $k \cdot p$ error and the latter the finite sampling

error. In all of this, we ignore any errors due to finite energy cut off or due to inadequacies of the pseudopotential.

5.2. The two sources of error

From previous sections we know that the error in the total energy can be approximated by the error in the eigenvalue sum for the fixed potential produced by the $k = 0$ states. We now formally divide this error into two components.

For any grid dimension, we can evaluate the eigenvalue sum using the $k \cdot p$ method. We will call this 'the $k \cdot p$ sum for that grid'. Similarly, for any grid we could evaluate the eigenvalue sum by full solution using all N planes waves. We will call this quantity 'the exact sum for that grid'. In both cases we use the self-consistent potential of the $k = 0$ states. Then we can define the '$k \cdot p$ error' for a particular grid as the difference between the $k \cdot p$ sum and exact sum for that grid. The 'finite sampling error' for a particular grid will be defined as the difference between the exact sum for that grid and the exact sum for an infinitely fine grid.

The $k \cdot p$ error is that error which the $k \cdot p$ method introduces for a particular grid whereas the finite sampling error would be present even if the eigenvalues were calculated exactly. We shall see later that as the grid dimension is increased, the finite sampling error tends to decrease but that the $k \cdot p$ error tends to increase. Ideally, one is searching for a grid size which reduces the finite sampling error whilst keeping the $k \cdot p$ error manageable and consequently minimizes the total error.

5.3. Errors in the total energy of fixed structure

In this section we concentrate on a fixed structure: FCC aluminium with a lattice parameter of 4.15 Å using the solutions at a single k-point ($k = 0$). As noted previously this gives an extreme test of the $k \cdot p$ method since the electronic states over a large Brillouin zone are generated from the solutions at a single point on the edge of the irreducible zone.

5.3.1. $k \cdot p$ errors. To evaluate the $k \cdot p$ error, we calculate the exact and $k \cdot p$ sum for a series of small grids up to 12^3 using the fixed self-consistent potential generated by the $k = 0$ states. The results are shown in table 5. As the grid size increases, some sampling points move further away from the point $k = 0$ and some sampling points move nearer to this point. In section 2 it was noted that the $k \cdot p$ error of a particular eigenvalue increases at least as fast as $|k|^2$. The result of this nonlinearity is that the $k \cdot p$ error increases with grid size. However the nature of the Monkhorst–Pack scheme is such that as the grid dimension increases, the successive increases in the maximum distance extrapolated get progressively less. Indeed the furthest that one must extrapolate is to the zone boundary itself. Consequently one would expect a $k \cdot p$ error that saturates at high grids. The results in table 5 show this. One can expect a maximum $k \cdot p$ error of around 0.6 eV in the energy of a fixed structure. The magnitude of this error can be reduced by a factor of four at no additional computational cost simply by using the k-point $(0.5, 0.5, 0.5)\pi/a$, thus halving the average extrapolation distance in the irreducible zone.

5.3.2. Finite sample errors. The finite sampling errors can be thought of as arising in two ways. The first is that numerically integrating a quadratic function using the trapezium rule will tend to underestimate the value of the integral. The second is that a finite

Table 5. Variation with respect to grid dimension of the $\mathbf{k} \cdot \mathbf{p}$ sum ($\Sigma eig_{k \cdot p}$), the exact sum (Σeig_{exact}) and the $\mathbf{k} \cdot \mathbf{p}$ error for FCC aluminium with lattice parameter 4.15 Å. The electronic potential is the self consistent potential produced by the occupied states at $\mathbf{k} = 0$.

Grid	$\Sigma eig_{k \cdot p}$ (eV)	Σeig_{exact} (eV)	$\mathbf{k} \cdot \mathbf{p}$ error (eV)
2^3	−34.823	−35.113	0.289
4^3	−35.059	−35.692	0.633
6^3	−35.425	−35.941	0.515
8^3	−35.421	−36.038	0.616
10^3	−35.375	−35.995	0.619
12^3	−35.350	−35.951	0.601

Table 6. Estimate of fintie sampling error ($\Sigma eig - \Sigma eig_{12}$) for FCC aluminium at a lattice parameter of 4.15 Å for series of k-point grids.

Grid	$\Sigma eig - \Sigma eig_{12}$ (eV)
1^3	6.546
2^3	0.838
4^3	0.259
6^3	0.009
8^3	−0.087
10^3	−0.044

number of k points will poorly describe the Fermi surface tending to overestimate the eigenvalue sum.

The first column of table 5 shows that exact sum (as defined previously) for various grids. It is clear from these figures that the definition of the Fermi surface is the most significant problem associated with finite sampling. If we take the value of the exact sum for 12^3 as an approximation to its value in the case of infinite sampling then one can calculate the finite sampling error as a function of grid size. This is done in table 6.

Consideration of the results in tables 5 and 6 suggests that the $\mathbf{k} \cdot \mathbf{p}$ method is a useful strategy for grids of up to 6^3. For this size grid the $\mathbf{k} \cdot \mathbf{p}$ error is around 0.6 eV and that of finite sampling is around 0.1 eV. After this the sampling error becomes small in comparison with the $\mathbf{k} \cdot \mathbf{p}$ error and increasing the grid size hardly affects the total error.

5.4. Errors in evaluation of energy differences

Up to now we have only considered the problem of the behaviour of the energy for a fixed structure. However for most problems it is energy differences between different systems which are important. We must now consider the behaviour of energy differences and their derivatives. In order to do this we must investigate the errors in the absolute energies described in section 5.3 and determine how they vary for different systems.

5.4.1. $\mathbf{k} \cdot \mathbf{p}$ errors.
Examination of the $\mathbf{k} \cdot \mathbf{p}$ error in energy differences can be achieved in the same way as in the previous section by comparison of the exact and $\mathbf{k} \cdot \mathbf{p}$ eigenvalue

Table 7. $k \cdot p$ sum ($\Sigma eig_{k \cdot p}$), exact sum (Σeig_{exact}) and $k \cdot p$ error for FCC aluminium at various lattice parameters and for grids of 2^3, 4^3 and 6^3.

Lattice parameter (Å)	$\Sigma eig_{k \cdot p}$ (eV)	Σeig_{exact} (eV)	$k \cdot p$ error (eV)
(a) Grid = 2^3			
3.77	−29.312	−29.574	0.262
3.82	−29.920	−30.182	0.262
3.90	−31.388	−31.652	0.264
3.95	−32.006	−32.273	0.267
4.15	−34.823	−35.113	0.290
4.20	−35.443	−35.739	0.296
4.29	−36.643	−36.953	0.310
4.34	−37.253	−37.570	0.317
(b) Grid = 4^3			
3.77	−29.777	−30.402	0.625
3.82	−30.351	−30.968	0.617
3.90	−31.750	−32.350	0.600
3.95	−32.337	−32.935	0.598
4.15	−35.059	−35.692	0.633
4.20	−35.682	−36.304	0.622
4.29	−36.910	−37.532	0.622
4.34	−37.533	−38.165	0.632
(c) Grid = 6^3			
3.77	−30.121	−30.664	0.543
3.82	−30.685	−31.223	0.538
3.90	−32.076	−32.588	0.512
3.95	−32.669	−33.172	0.503
4.15	−35.425	−35.941	0.516
4.20	−36.039	−36.551	0.512
4.29	−37.233	−37.767	0.534
4.34	−37.842	−38.385	0.543

sum for a series of grids and a series of structures. This has been done for grids of 2^3, 4^3 and 6^3 at eight different lattice parameters. The results are shown in table 7.

Table 7 shows that the $k \cdot p$ error has the same sign for all the lattice parameters. Consequently these errors will partially cancel when calculating energy differences. Table 7(a) shows the variation of the error with respect to lattice parameter for small grids. It is clear that the error increases with increasing lattice parameter. This is easily understood in terms of two distinct effects. Firstly, in all cases using the $k \cdot p$ method one solves using 19 bands. However for the lowest lattice parameter the full solution uses 131 plane waves whereas the largest lattice parameter uses 179 plane waves. Hence, for the lowest lattice parameter the restriction of 19 bands is less severe but the larger the lattice parameter the larger the error. Secondly the larger the lattice parameter the smaller is any particular reciprocal lattice vector. In the present system this increases the magnitude of {100} components of the pseudopotential so that the band structure becomes more perturbed from the free-electron form. The result is that the $k \cdot p$ matrix

Table 8. Estimate of the finite sampling error at a series of grids for a range of lattice parameters. E_N is the exact sum for a Monkhorst–Pack k-point grid of dimension $N \times N \times N$.

Lattice parameter (Å)	$E_1 - E_6$ (eV)	$E_2 - E_6$ (eV)	$E_4 - E_6$ (eV)
3.77	7.864	1.090	0.262
3.82	7.665	1.041	0.254
3.90	7.416	0.936	0.238
3.95	7.212	0.899	0.236
4.15	6.536	0.828	0.249
4.20	6.384	0.812	0.247
4.29	6.159	0.814	0.235
4.34	6.043	0.815	0.220

elements between the bands we take and those that we ignore increases and the error in the **k** · **p** method must increase.

As we move to bigger grids, the error for each lattice parameter increases in much the same way as it did for the 4.15 Å case. However, there is a tendency for the error at very low lattice parameters to increase more than that at intermediate values. This effect is simply that for low lattice parameters the zone boundary is further away and so the extrapolation error is larger. This effect only becomes apparent for large grids since near the origin the **k** · **p** error varies as k^2 and higher order terms only become important further away.

The results show that for the 6^3 grid the **k** · **p** error of 0.6 eV in the absolute energy has been reduced to a maximum **k** · **p** error of 0.040 eV in energy differences. This being the error in calculating the energy difference between the 4.15 Å structure and either the 3.77 Å or the 4.34 Å structure. The actual energy differences between these pairs of structures are 0.4445 eV and 0.4216 eV respectively, giving a **k** · **p** error of around 10%. Using the k-point $(0.5, 0.5, 0.5)\pi/a$ reduces **k** · **p** errors by a factor of four. The maximum **k** · **p** error in energy differences is then around 0.01 eV which is 2% of the energy difference.

5.4.2. Finite sampling errors. There is no reason to assume that the finite sampling error will cancel from structure to structure to the same extent as the **k** · **p** error and so it is necessary to evaluate the degree of cancellation exactly. The most direct method of doing this would be to repeat the full solutions of table 5 for all lattice parameters. To do this for grids of up to 12^3 is a rather time consuming process. Instead we attempt a short cut. Using the data of table 7 we approximate the exact sum for infinite sampling as equal to the exact sum for the 6^3 grid. Table 8 shows the finite sampling error with respect to lattice parameter and grid size. For a given grid size the finite sampling error is roughly proportional to $1/a^2$, which is proportional to the kinetic energy of the occupied states. The lattice parameter varies by 15% over the structures studied so that the finite sampling error in energy differences should be equal to around 30% of the sampling error for a fixed structure. For the 6^3 grid the true sampling error in the energy of the 4.15 Å cell 0.009 eV but inspection of table 6 shows that this is somewhat fortuitous. A figure of around 0.1 eV more truly reflects the trend. Using this value one would expect an error in energy differences due to finite sampling of around 0.03 eV. The corresponding values for 1^3, 2^3, 4^3 grids being 2 eV, 0.25 eV and 0.08 eV, respectively.

The results again suggest that a grid size of 6^3 is the largest justified for this particular situation. For this size of grid the finite sampling error and the $k \cdot p$ error become comparable and the total error is minimized. It should also be noted that moving from total energies to energy differences, the $k \cdot p$ error has been diminished more than the finite sampling error.

6. Run times

The potential usefulness of the $k \cdot p$ method is the degree to which it reduces the run times of otherwise very lengthy calculations so that previously intractable calculations become tractable. The calculations presented in this paper are not particularly time consuming and could have been adequately treated by standard non $k \cdot p$ methods. They were chosen purely for reasons of simplicity on the basis that the conclusions of the analysis can be easily extrapolated to more complex systems.

A total energy $k \cdot p$ calculation executes in two stages. In the first stage exact eigenstates are calculated self-consistently at a reduced number of k-points and in the second stage approximate solutions are calculated at a full set of k-points. The run time may be dominated by either the first or second stage of the calculation. The first stage will dominate in calculations with very high cut-off energies, with small numbers of $k \cdot p$ k-points or in which no self-consistency iterations are required in the second stage of the $k \cdot p$ method, such as the calculations described in this paper. The computational time will be dominated by the second stage of the $k \cdot p$ method when $k \cdot p$ solutions are generated at a large number of k-points or when many self-consistency iterations are needed. The saving in computational time depends on which stage of the calculation dominates. These two limits are discussed below.

6.1. Second stage of calculation dominates

In the past, calculations would be performed by generating self-consistent solutions at all k-points considered. The time taken for this could be written $N_k t_0$ where t_0 is the time to generate a self-consistent solution at one k-point and N_k is the number of k-points used in the calculation. We shall ignore any variation in the time taken for self-consistency at each k-point with the number of k-points included in the calculation. When the time taken for the $k \cdot p$ method is dominated by the time taken for the second stage the total time taken is $N_k t_1$ where t_1 is the time taken to generate a self-consistent solution at one k-point using the $k \cdot p$ method. In this case the $k \cdot p$ method is quicker than a full calculation by a factor of t_0/t_1. This ratio is typically several orders of magnitude.

6.2. First stage of calculation dominates second stage

If there are fewer k-points or if the structure is more nearly free electron like computational time of the $k \cdot p$ method will be dominated by the first stage. The run time is then simply that required to generate the solutions at the reduced number of k-points. In the case considered in this paper this requires the solutions for 19 bands rather than the 7 that are actually occupied or partially occupied so that the computational time required is of the order $3t_0$. The non $k \cdot p$ method must solve using all the plane wave basis states whose energies lie below the cut-off energy at each of the N_k k-points. However, only the occupied or partially occupied bands need be considered. Hence a

time $N_k t_0$ is required for the conventional calculation. The gain of the **k · p** method in this case is $N_k/3$.

For the examples situations considered in this paper the number of k-points in the irreducible wedge of the Brillouin zone is fairly small because the structures all have cubic symmetry. The time saved by using the **k · p** method in this case is fairly modest. For larger numbers of k-points, however, the fractional and absolute time savings become crucial.

7. Conclusion

The computational implementation of the **k · p** method has been demonstrated to be straightforward and fast. For the structures considered and the grid used the method has been shown to be subject to an error of around 0.04 eV in calculating energy differences of around 0.5 eV that is an error of about 10%. It should be noted that this error could be reduced by a factor of four with no increase in computation time by using the point $k = (0.5, 0.5, 0.5)\pi/a$ rather than $k = 0$ for the initial calculation. Although the time saving offered by the **k · p** method is relatively small for the particular calculations presented in this paper, for many calculations the saving in computational time will be typically several orders of magnitude.

The technique of using a different number of k-points for calculating the electronic potential and for calculating the electronic eigenvalues has been shown to be particularly efficient in the present case. Such a technique is not restricted to the **k · p** method and may be applicable in a wide range of systems at a considerable saving of computational time.

Further work needs to be undertaken in order to investigate how the results of this work should be modified for different sized Brillouin zones and for comparing total energies between structures whose Brillouin zones have different shapes. One should also like to investigate the possibility of performing **k · p** expansions about not one, but a coarse grid of k-points. Although the **k · p** method is an approximate method, it is a controlled approximation in the sense that by suitable choice of parameters one may trade off accuracy against speed to an arbitrary extent. Further work needs to be performed in order to assess the optimal choice of parameters. Finally the results presented in this paper show that the **k · p** error is rather predictable in many ways. It is always positive and it increases roughly quadratically with increasing extrapolation distance. Work is already in progress to estimate the magnitude of the error in any particular calculation so that the accuracy of the **k · p** method can be significantly improved.

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References

Ashcroft N W and Mermin N D 1976 *Solid State Physics* (Tokyo: Holt Saunders) p 113

Baldereschi A 1973 *Phys. Rev.* B **7** 5212
Car R and Parrinello M 1985 *Phys. Rev. Lett.* **55** 2471
Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
Chadi D J and Cohen M L 1973 *Phys. Rev.* B **8** 5747
Cheng C, Needs R J, Heine V and Churcher N 1987 *Europhys. Lett.* **3** 475
Fu C L and Ho K M 1983 *Phys. Rev.* B **28** 5480
Goodwin L, Needs R J and Heine V 1990 *J. Phys.: Condens. Matter* **2** 351
Harris J 1985 *Phys. Rev.* B **31** 1770
Harrison W 1970 *Solid State Theory* (New York: McGraw Hill) p 140
Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
Payne M C, Joannopoulos J D, Allan D C, Teter M P and Vanderbilt D H 1986 *Phys. Rev. Lett.* **56** 2656
Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048