Tests of the Harris energy functional

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Abstract. Tests of the Harris energy functional are presented for a number of different systems, using the pseudopotential total energy method within local density theory. Using an input charge density consisting of a superposition of pseudo-atomic charge densities we evaluate the Harris and Kohn–Sham energy functionals and compare with the self-consistent results. We calculate the lattice constant, bulk modulus and some phonon frequencies of silicon and the aluminium (111) surface energy. For the bulk properties of silicon both functionals yield good agreement with the self-consistent results without the need for self-consistency. For the aluminium surface energy neither functional agrees well with the self-consistent solution. However, for a range of input charge densities the Harris functional consistently gives *better* results than the Kohn–Sham functional. This result is explained in terms of the long-wavelength instability encountered in solving the Kohn–Sham equations.

1. Introduction

Density functional theory (Hohenberg and Kohn 1964) has proved a very useful theoretical foundation of quantum mechanical methods for calculating total energies. A number of review articles may be consulted for detailed discussions of the theory (for example Kohn and Vashishta 1983, Callaway and March 1984). The central results of density functional theory are that the ground-state total energy of a system of interacting particles is a functional of the ground-state particle density and that this energy functional is minimised by the correct density. For practical applications density functional theory is often recast within the Kohn–Sham formalism (Kohn and Sham 1965) in which one is required to solve single-particle Schrödinger equations (known as Kohn–Sham equations) to calculate the total energy. In practical applications the local density approximation to the exchange–correction energy has proved useful for systems of interacting electrons. Such density functional theory calculations, formulated within Kohn–Sham theory and using the local density approximation, have been performed on a large number of systems. Although the use of the local density approximation leads to large errors in some cases there are many other cases in which excellent agreement with experimental results has been obtained (see the review article by Williams and von Barth 1983).

There are many technical problems involved with large-scale applications of the Kohn–Sham formulation of density functional theory. In this paper we will test a scheme that was originally proposed by Harris (1985) in order to simplify such calculations. Some tests of the Harris functional have been reported before (Harris 1985, Polatoglou and Methfessel 1988, Foulkes and Haydock 1989) showing that this method can yield

excellent results and is worthy of a more complete investigation. In this paper we report tests of the Harris functional on a number of different physical systems, illustrating both the strengths and weaknesses of the method.

An important advantage of density functional theory is the existence of a stationary principle for the total energy. This principle guarantees that the error in the total energy is second order in the deviation of the trial charge density from the exact form. In practice this means that it is often possible to obtain accurate estimates of the total energy using approximate trial charge densities. The basic point is that there are many different energy functionals that are stationary at the true ground-state charge density and some may be more convenient to calculate than others. The Harris functional that we shall study in this paper has a particularly convenient form for reasons that we will discuss later. A disadvantage of the Harris functional over the standard expression is that although the Harris form is stationary at the exact charge density it is not necessarily minimised by the exact charge density. In practice this may cause some problems because one can no longer be sure that a different trial charge density that lowers the calculated total energy is in fact closer to the exact solution. This point was recognised by Harris (1985) and has been discussed more fully by Foulkes and Haydock (1989).

The main aim of this paper is to test the accuracy of the Harris energy functional for a range of properties and systems. The Harris functional is tested against the standard energy functional (which we shall call the Kohn–Sham functional) and against the numerically exact solution (which we shall call the self-consistent solution) calculated within the local density approximation. The subsidiary aim of this paper is to test approximate forms of the charge density for different systems. We will test whether a charge density consisting of a superposition of pseudo-atomic charge densities is sufficiently close to the exact charge density to give accurate results for a range of properties of different systems when used in conjunction with the Harris and Kohn–Sham energy functionals.

2. The Kohn–Sham formulation of density functional theory

In this section we give a brief mathematical summary of the Kohn–Sham formulation of density functional theory. For a derivation of these formulae we refer the reader to the articles by Kohn and Vashishta (1983) and Callaway and March (1984). The Kohn–Sham equations are

$$\{-\tfrac{1}{2}\nabla^2 + V[n(r)]\}\varphi_i(r) = \varepsilon_i\varphi_i(r) \tag{1}$$

where the ith single-particle orbital is denoted by $\varphi_i(r)$ and ε_i is the corresponding eigenvalue. The potential $V[n(r)]$, which is a function of r only, is given by

$$V[n(r)] = V_n(r) + V_H[n(r)] + \mu_{XC}[n(r)] \tag{2}$$

where V_n is the potential due to the nuclei, V_H is the electron Hartree potential, μ_{XC} is

the exchange–correlation potential and $n(r)$ is the electronic charge density. The charge density $n(r)$ is given by

$$n(r) = \sum_i |\varphi_i(r)|^2 \tag{3}$$

where the summation is over all occupied orbitals. The exchange–correlation potential, μ_{XC}, is related to the exchange–correlation energy, E_{XC}, by

$$\mu_{XC}[n(r)] = \delta E_{XC}[n(r)]/\delta n(r) \tag{4}$$

and the total energy, E, is given by

$$E[n] = \sum_i \int d^3r \, \varphi_i(r)^* (-\tfrac{1}{2}\nabla^2)\varphi_i(r)$$

$$+ \int d^2r \, V_n(r)n(r) + E_H[n(r)] + E_{XC}[n(r)] + E_{nn} \tag{5}$$

where the first term on the right-hand side of (5) is the kinetic energy of a non-interacting system of electrons of density $n(r)$, E_H is the electron Hartree energy and E_{nn} is the interaction between the nuclei. Often one uses the local density approximation for E_{XC}, which is given by

$$E_{XC}[n(r)] = \int d^3r \, \varepsilon_{SC}(n(r))n(r) \tag{6}$$

where $\varepsilon_{XC}(n(r))$ is the exchange–correlation energy per electron of a homogeneous electron gas of density $n(r)$, which is known accurately over a wide range of densities from diagrammatic (Hedin and Lundqvist 1971) and quantum Monte Carlo (Ceperley and Alder 1980) calculations.

Equations (1) to (6) form a complete prescription for calculating the total energy. The problem is a self-consistent one—the potential entering the Kohn–Sham equations depends on the charge density $n(r)$ which in turn is determined by the solutions of the Kohn–Sham equations.

3. The Harris and Kohn–Sham energy functionals

First of all we shall describe a procedure for solving the Kohn–Sham equations self-consistently that uses the charge density as the basic variable. One obtains a trial charge density $n_{in}(r)$ and uses equation (2) to calculate the potential $V[n(r)]$ that appears in the Kohn–Sham equations (1). The Kohn–Sham equations are then solved yielding the eigenfunctions $\varphi_i(r)$ and the corresponding eigenvalues ε_i. The eigenfunctions are used to construct the output charge density, $n_{out}(r)$, from equation (3) and the total energy is obtained using the eigenvectors $\varphi_i(r)$ and the output charge density in equation (5). In general the output charge density so obtained, n_{out}, is not equal to the original trial charge density, n_{in}, and so a new trial charge density must be calculated, possibly as some linear combination of n_{in} and n_{out}, and the procedure repeated until self-consistency is achieved, at which point $n_{in} = n_{out}$. To be accurate this method actually finds a stationary point of the energy functional which need not be the global minimum, but in practical applications one does in fact appear to obtain the global minimum.

After any iteration of the self-consistency process the total energy may be calculated using equation (5). The value of the energy will only be correct when self-consistency has been reached but a good approximation may well be achieved without iteration or

after a small number of iterations. In the standard approach the energy is calculated using the Kohn–Sham energy functional of equation (5) which we can rewrite as

$$K = \sum_i \varepsilon_i - E_H[n_{out}(r)] + E_{XC}[n_{out}(r)] - \int d^3r \, \mu_{XC}[n_{out}(r)]n_{out}(r) + E_{nn}$$

$$+ \int d^3r \{V[n_{out}(r)] - V[n_{in}(r)]\}n_{out}(r) \tag{7}$$

where we have used the Kohn–Sham equations (1) to eliminate the kinetic energy term. This expression is both minimal and stationary with respect to errors in the charge density n_{out}, i.e.

$$K = E[n] + O[(n_{out} - n)^2] + \text{higher-order tems} \tag{8}$$

where $E[n]$ is the exact energy which is a functional of the exact ground-state charge density n and $O[(n_{out} - n)^2]$ indicates a term of order $(n_{out} - n)^2$ which is always positive (as is the sum of all correction terms to $E[n]$). Harris (1985) suggested that in some cases the Kohn–Sham functional would be inconvenient to calculate because it requires a knowledge of n_{out} and the solution of Poisson's equation for n_{out}. Harris suggested that a more convenient form would be

$$H = \sum_i \varepsilon_i - E_H[n_{in}(r)] + E_{XC}[n_{in}(r)] - \int d^3r \, \mu_{XC}[n_{in}(r)]n_{in}(r) + E_{nn} \tag{9}$$

which we shall call the Harris energy functional and denote by H. Harris (1985) proved that this form of the energy is stationary (but not minimal) with respect to errors in the charge density. The Harris functional satisfies the following relationship:

$$H = E[n] + O[(n_{out} - n)(n_{in} - n)] + \text{higher-order terms}. \tag{10}$$

Note that the lowest-order error term for the Harris functional, which can be of either sign, is of order $(n_{out} - n)(n_{in} - n)$ and it is by no means clear that this should be larger than the error term for the Kohn–Sham functional. Although the Harris form (9) requires the solution of the Kohn–Sham equations for the potential generated by n_{in}, to obtain the eigenvalues ε_i, it does not require the construction of the output charge density n_{out} or the solution of Poisson's equation for n_{out}. For some calculational methods this may be a very great advantage, particularly in methods using local orbital basis sets. The calculations reported in this paper use the total energy pseudopotential method and a plane-wave basis set and in this case the calculation of n_{out} is straightforward. Our main aim was to test the Harris functional for applications in techniques where n_{out} is difficult to calculate, although in fact we will find that the Harris functional may be of use even when n_{out} can readily be calculated.

4. Tests of the Harris and Kohn–Sham energy functionals

We have performed a number of tests of the Harris and Kohn–Sham energy functionals. In each case we have compared the energies calculated using these functionals with the energies from self-consistent calculations. The calculations were performed using the total energy pseudopotential method with norm-conserving pseudopotentials (Hamann *et al* 1979), constructed using the algorithm due to Kerker (1980), and a plane-wave expansion for the wavefunctions and potentials. For a review of this technique see the

Table 1. Results for silicon in the diamond structure. The table gives the calculated values of the total energy at the experimental equilibrium lattice constant of 5.429 Å, the calculated equilibrium lattice constant, bulk modulus, TO(Γ) phonon frequency and TA(X) phonon frequency. In each case the total energies were calculated from the Harris functional, H, and the Kohn–Sham functional, K, using a superposition of pseudo-atomic charge densities for n_{im} and from a self-consistent calculation giving E.

	Harris using H	Kohn–Sham using K	Self-consistent using E
Total energy (eV)	-108.03	-107.88	-107.91
Deviation from E-result	-0.11%	$+0.03\%$	
Lattice constant (Å)	5.335	5.415	5.397
Deviation from E-result	-1.1%	$+0.3\%$	
Bulk modulus (Mbar)	1.027	0.967	0.983
Deviation from E-result	$+4.5\%$	-1.6%	
TO(Γ) frequency (THz)	15.17	15.38	15.31
Deviation from E-result	-0.9%	$+0.45\%$	
TA(X) frequency (THz)	4.69	4.55	4.48
Deviation from E-result	$+4.7\%$	$+1.5\%$	

article by Ihm (1988). In each case we have taken a superposition of neutral pseudo-atomic charge densities for the trial charge density, n_{in}, i.e.

$$n_{in}(\mathbf{r}) = \sum_{\alpha} n_{atomic}(\mathbf{r} - \mathbf{R}_{\alpha}) \tag{11}$$

where $\mathbf{R}_{\alpha}$ is the position vector of the αth atom. The pseudo-atomic charge densities were obtained from self-consistent calculations of the charge density of non-spin-polarised atoms in their ground-state configurations using the same pseudopotentials as in the bulk calculations.

Our first test case was silicon in the diamond structure. We calculated the energy as a function of volume for fifteen volumes in the range $0.857V_0$ to $1.158V_0$, where $V_0 = 20.002$ Å^3 and is the experimental equilibrium volume per atom. A basis set including all plane waves with kinetic energy up to 15 Ryd was used and the Brillouin zone integrations were performed with a special-points technique sampling ten points in the irreducible wedge of the first Brillouin zone. In each case the energies were calculated using the Harris energy functional, H, and Kohn–Sham energy functional, K, with the overlapping pseudo-atomic charge density for n_{in}. The calculation was then taken to self-consistency in order to calculate the converged energy E. The calculated energies were fitted to the Murnaghan equation of state (Murnaghan 1944) to obtain the bulk modulus and lattice constant. The results are given in table 1, together with the percentage errors from the self-consistent results. These results indicate that the energies calculated using the superposition of pseudo-atomic charge densities for n_{in} are accurate enough to obtain excellent values for the lattice constant and bulk modulus of silicon. This is in accordance with the results of Polatoglou and Methfessel (1988) who performed calculations on several materials, including silicon, and compared the cohesive energy, lattice constant and bulk modulus calculated from the Harris functional with the self-consistent results. We should also note that our self-consistent results are close to the
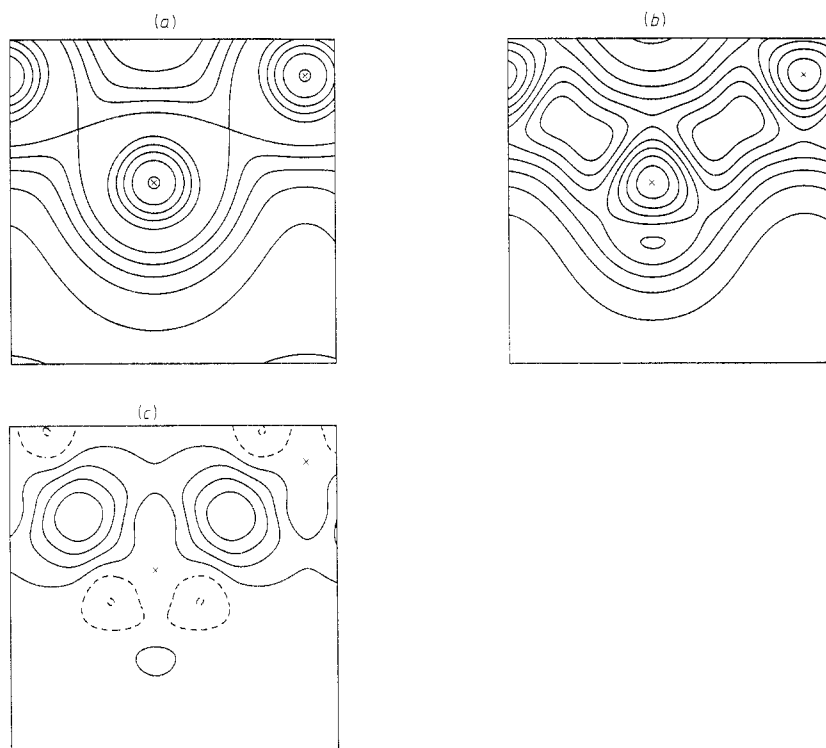
Figure 1. Contour plots of the pseudo-charge density of silicon in the (110) plane. (a) The superposition of pseudo-atomic charge densities, n_{in}. (b) The self-consistent charge density, n. (c) The difference between the self-consistent charge density and the superposition of pseudo-atomic charge densities. $n - n_{in}$. The contour spacing is 1.5 electrons/atom for (a) and (b) and 1 electron/atom for (c). The positions of the atoms are indicated by crosses and the broken curves in (c) indicate negative values.

experimental ones, the experimental lattice constant of silicon being 5.429 Å and the experimental bulk modulus being 0.98 Mbar (*Landolt–Börnstein* 1982). In each case the error in the quantities calculated with the Harris functional is about three times that using the Kohn–Sham functional.

Contour plots of the superposition of pseudo-atomic charge densities, n_{in}, the self-consistent charge density, n, and the difference between them, $n - n_{in}$, are shown in figures 1(a), 1(b) and 1(c) respectively. The plots are sections in the (110) plane passing through the zig-zag chains of atoms. One can see from these plots that the major difference between the superposition of pseudo-atomic charge densities and the self-consistent charge density is the build up of charge between the atoms in the self-consistent solution. These 'bond charges' are roughly spherical and lie half-way between the atoms. This feature could easily be included in a new trial charge density which would presumably yield better agreement with the self-consistent results than the superposition of pseudo-atomic charge densities.

Our next calculations were for phonon frequencies of silicon. Calculations of phonon frequencies in silicon by Wendel and Martin (1979) have already indicated that non-self-consistent calculations (but using the variational principle) may give reasonable results, but the details of their calculations were somewhat different from those presented in

Table 2. Results for the aluminium bulk and (111) surface calculations. The table gives the calculated values of the energy per atom for the bulk, the energy per atom for a calculation with a unit cell consisting of nine layers of aluminium and six layers of vacuum and the resulting values of the surface energy. In each case the total energies were calculated using the Harris functional, H, and the Kohn–Sham functional, K, with a superposition of pseudo-atomic charge densities for n_{in} and from a self-consistent calculation giving E.

	Harris using H	Kohn–Sham using K	Self-consistent using E
Bulk Al (eV/atom)	−57.102	−57.089	−57.089
Deviation from E-result	−0.02%	+0.001%	
Nine-layer slab Al (eV/atom)	−57.083	−57.770	−56.997
Deviation from E-result	−0.15%	+2.2%	
Surface energy (eV Å^{-2})	0.013	0.848	0.060
Deviation from E-result	−78%	+1300%	

this paper. Our approach was to calculate the energy, again using the superposition of pseudo–atomic charge densities for n_{in}, as a function of the atomic displacements. The resulting energy–displacement curves were fitted to Chebyshev polynomials to calculate the second derivatives at zero displacement which gives the phonon frequencies. We did this for the TO(Γ) mode using a third-order Chebyshev polynomial and for the TA(X) mode using a second-order Chebyshev polynomial. A basis set containing all plane waves up to 15 Ryd in energy was used, sampling 5 k-points in the irreducible wedge of the Brillouin zone for the TO(Γ) mode and 48 k-points for the TA(X) mode. The results are given in table 1. The self-consistent calculations gave phonon frequencies of 15.31 THz for the TO(Γ) mode and 4.48 THz for the TA(X) mode which are in good agreement with the experimental results of 15.3 THz and 4.5 THz respectively (*Landolt–Börnstein* 1982). We conclude that the energies calculated using the superposition of pseudo-atomic charge densities for n_{in} are also accurate enough for obtaining excellent values for the TO(Γ) and TA(X) phonon frequencies of silicon. In both cases the errors in the quantities calculated with the Harris functional are a little larger than those obtained using the Kohn–Sham functional.

A simple way of improving the trial charge density for these cases can be devised by using the idea of 'bond charges' mentioned above. According to the bond charge model developed by Martin (1969) the bond charges are built up by scattering of the electrons from the nearest-neighbour ion cores and thus they should be approximately half-way between nearest neighbours even when the atoms are displaced. This idea could be used to obtain a trial charge density for the systems with displaced atoms.

We have also performed a set of calculations on a rather different material, aluminium, in order to calculate the (111) surface energy. We started with a calculation for bulk aluminium in the FCC structure with the zero-temperature lattice constant of 4.02 Å. To facilitate comparison we performed this calculation in the same unit cell as the surface calculation, consisting of a cell containing fifteen close-packed layers in a (111) orientation. A basis set containing all plane waves up to 12 Ryd in energy was used and for the Brillouin zone integration we sampled 37 k-points in the irreducible wedge. Again we used the superposed pseudo-atomic charge densities for n_{in} and calculated the Harris and Kohn–Sham energies and the self-consistent energy. The results are given in table 2. For bulk aluminium the energies calculated using n_{in} are extremely close to the
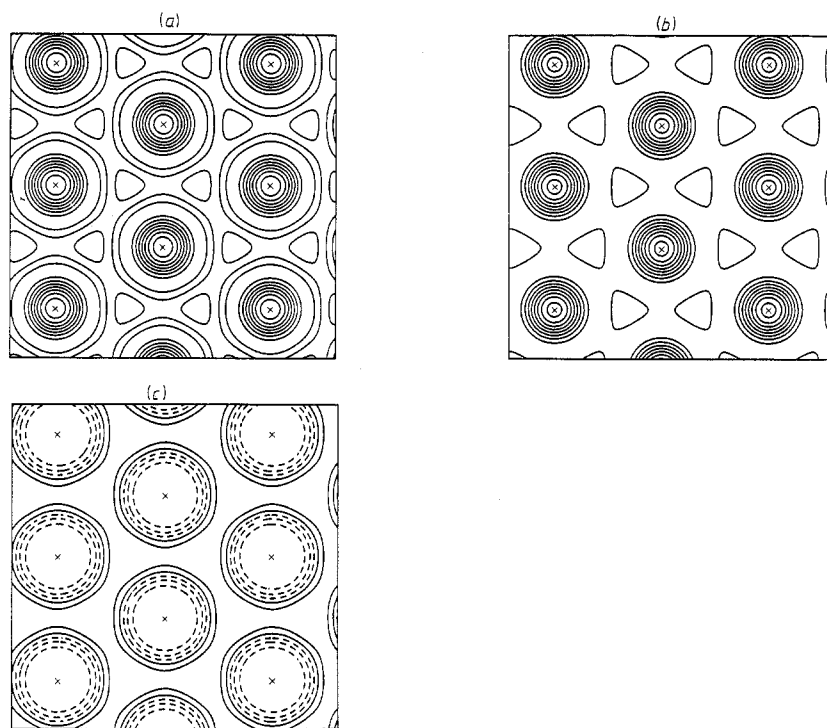
Figure 2. Contour plots in the (111) plane of the pseudo-charge density of bulk FCC aluminium. (a) The superposition of atomic charge densities, n_{in}. (b) The self-consistent charge density, n. (c) The difference between the self-consistent charge density and the superposition of atomic charge densities, $n - n_{in}$. The contour spacing is 0.2 electrons/atom. The positions of the atoms are indicated by crosses and the broken curves in (c) indicate negative values.

self-consistent energy. The charge-density plots of the superposed pseudo-atomic charge densities, the self-consistent charge density and the difference between then, $n - n_{in}$, are shown in figures 2(a), 2(b) and 2(c) respectively. From these plots one can see that the most significant difference between the superposed pseudo-atomic charge densities and the self-consistent density is that, in forming the solid, charge moves radially outwards from the atoms to form a more uniform charge density. This could easily be modelled by isotropically dilating the individual atomic charge densities by a suitable amount.

For the surface calculation we used the same size of unit cell as for the bulk calculation, but containing nine layers of aluminium and the equivalent of six layers of vacuum. We used the same basis set energy cut-off and Brillouin zone integration as for the bulk calculation. The energies obtained from these calculations and the resulting surface energies, calculated from the difference between surface and bulk energies, are given in table 2. The differences between the values calculated using the superposed pseudo-atomic charge densities and the self-consistent results leads to large errors in the surface energy. The error of 78% in the surface energy obtained using the Harris functional derives mainly from the error in the surface calculation where the energy is 0.086 eV per atom too low. The very large error of 1300% in the surface energy calculated with the Kohn–Sham functional also derives from the error in the surface calculation, but in this

Table 3. Results for the aluminium (111) surface. The table gives the values calculated for the energy using the Harris functional, H, and the Kohn–Sham functional, K, and the percentage error from the self-consistent result. The four calculations presented correspond to four different input charge densities of increasing accuracy.

Calculation number	Energy from H (eV/atom) (% error from E)	Energy from K (eV/atom) (% error from E)
1	−57.083 (−0.15%)	−55.770 (+2.2%)
2	−57.009 (−0.022%)	−56.918 (+0.13%)
3	−57.003 (−0.011%)	−56.977 (+0.035%)
4	−57.000 (−0.005%)	−56.990 (+0.011%)

case the energy was 1.227 eV per atom higher than the self-consistent result. Clearly the superposition of pseudo-atomic charge densities is not an adequate input charge density for calculating the surface energy using either the Harris or the Kohn–Sham energy functionals. However, the surface energy calculated with the Harris functional was considerably closer to the self-consistent result than the energy from the Kohn–Sham functional. We decided to investigate whether this was also the case for input charge densities that were closer to the self-consistent one. To obtain charge densities that were closer to the self-consistent result we used linear combinations of n_{in} and n_{out} obtained from intermediate cycles of the self-consistent calculation. The results are given in table 3. Note that in each case the result from the Harris functional is closer to the self-consistent result than the Kohn–Sham result. We shall attempt to understand this important phenomenon in the next section of this paper.

The charge-density plots for the superposed pseudo-atomic charge densities, the self-consistent charge density and the difference between them for the surface calculation are shown in figures 3(a), 3(b) and 3(c) respectively. Note that the surface plots are sections in the (11$\bar{1}$) plane which is not perpendicular to the (111) surface. The reason for this choice was to facilitate comparison with the bulk charge densities of figure 2 which are sections in the close-packed (111) plane. There appear to be two points of interest to be gained from these plots. Firstly, by comparison of figures 2(b) and 3(b) one can see that the charge density returns rapidly to the bulk form in the interior of the metal. Even one atomic layer away from the surface the charge density is remarkably close to the bulk self-consistent result. This is because the screening length in aluminium is very short (about 0.5 Å which is to be compared with the separation between atomic layers in the (111) direction of 2.32 Å). The second point of interest is that the major difference between the superposed pseudo-atomic charge densities (figure 3(a)) and the self-consistent charge density (figure 3(b)) is the smoothing of the charge density in the plane of the surface in the self-consistent result. It appears that this feature of the charge density must be included in a trial charge density used for calculating the surface energy.

5. Analysis of the long-wavelength behaviour in jellium

In this section we investigate the size of the error terms in the Harris and Kohn–Sham energy functionals for a calculation on jellium. The exact solution is of course a constant
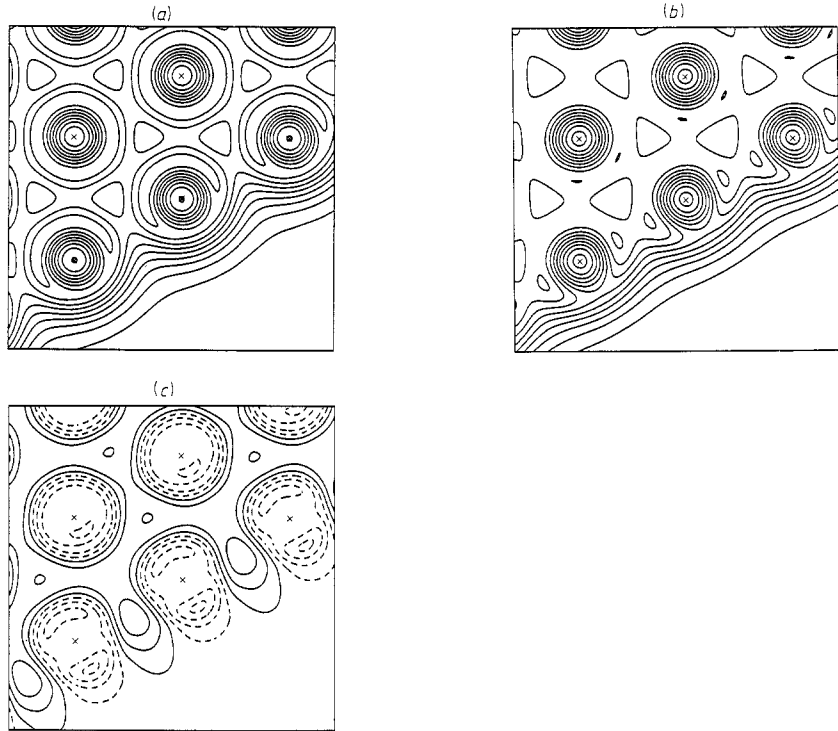
Figure 3. Contour plots of the pseudo-charge density at the (111) surface of aluminium. Note that the plots are in the (111 plane which is not perpendicular to the surface. (*a*) The superposition of atomic charge densities, n_{in}. (*b*) The self-consistent charge density, n. (*c*) The difference between the self-consistent charge density and the superposition of atomic charge densities, $n - n_{in}$. The contour spacing is 0.2 electrons/atom. The positions of the atoms are indicated by crosses and the broken curves (*c*) indicate negative values.

charge density, n_0, but we shall imagine performing a calculation using an approximate charge density n_{in}. We will work in a unit cell that is long and thin, being of length $2\pi/q_0$ in the z direction, where q_0 is small. Suppose that we use a trial charge density given by

$$n_{in}(\mathbf{r}) = n_0 + a \cos(q_0 z) \tag{12}$$

where a is small. The trial charge density gives a Hartree potential, V_H, which in reciprocal space as a function of wavevector $\mathbf{q}$ is given by

$$V_H(\mathbf{q}) = (4\pi a/q_0^2)\tfrac{1}{2}\delta(q_x)\delta(q_y)(\delta(q_z - q_0) + \delta(q_z + q_0)). \tag{13}$$

There will also be an exchange–correlation potential generated by the sinusoidal term in the trial charge density, but we will neglect this. To calculate the output charge density we use the Thomas–Fermi density response function $X(\mathbf{q}) = -g(E_F)$ where $g(E_F)$ is the density of states per unit volume at the Fermi energy. Of course we should use the density response function of the Kohn–Sham electrons but the Thomas–Fermi form should be a good approximation to this in the long-wavelength limit. This leads to

$$n_{out} = n_0\delta(\mathbf{q}) + X(\mathbf{q})V_H(\mathbf{q})$$

$$= n_0\delta(\mathbf{q}) - g(E_F)(4\pi a/q_0^2)\tfrac{1}{2}\delta(q_x)\delta(q_y)(\delta(q_z - q_0) + \delta(q_z + q_0)). \tag{14}$$

We can now write down the form of the lowest-order error terms in the Kohn–Sham and Harris energy functionals. The Kohn–Sham function has an error

$$K - E[n] = O[(n_{out} - n)(n_{out} - n)] + \text{higher-order terms}$$

$$= O[(n_{in} - n)(n_{in} - n)/q_0^4] + \text{higher-order terms} \quad (15)$$

and the Harris functional has an error

$$H - E[n] = O[(n_{out} - n)(n_{in} - n)] + \text{higher-order terms}$$

$$= -O[(n_{in} - n)(n_{in} - n)/q_0^2] + \text{higher-order terms}. \quad (16)$$

We can draw two conclusions from this analysis. Firstly, when the unit cell is long, so q_0 is small, then the error term for the Harris functional, which diverges like $1/q_0^2$, should be smaller than the error term for the Kohn–Sham functional which diverges like $1/q_0^4$. Secondly, the Harris functional should *underestimate* the energy because the error term in equation (16) is negative, whereas the Kohn–Sham function should *overestimate* the energy because the error term in equation (15) is positive. This means that the Harris functional should actually be maximal at the correct charge density. Table 3 shows exactly this behaviour for the aluminium surface calculations. In each case the energy from the Harris functional is closer to the self-consistent result than the Kohn–Sham functional and in each case the Harris functional underestimates the energy while the Kohn–Sham functional overestimates it. We believe that this phenomenon is due to the same kind of long-wavelength behaviour that we have found in the simple model studied in this section, in which the long-wavelength instability arises from the form of the dielectric response function at low q.

6. Conclusions

We have compared results obtained with the Kohn–Sham and Harris energy functionals for a variety of physical properties of silicon and aluminium. Using an input charge density formed from superposing pseudo-atomic charge densities in conjunction with either the Kohn–Sham or Harris functional gives excellent values for the energies of bulk silicon and aluminium. We have shown that the superposition of pseudo-atomic charge densities is sufficiently close to the self-consistent charge density to allow accurate calculation of quantities such as the bulk modulus and phonon frequencies of silicon. For bulk properties the error using the Kohn–Sham functional was typically about a third of that from using the Harris functional. For each of our calculations we have attempted to indicate the major differences between the self-consistent charge densities and the superposed pseudo-atomic charge densities. We find that, for the systems we have studied, these differences are of a rather simple kind and we believe that it should be straightforward to include these effects in new trial charge densities.

An input charge density of superposed pseudo-atomic charge densities was not adequate for calculating the surface energy of aluminium using either the Harris or the Kohn–Sham functionals. We found that the error in the surface energy was much larger for the Kohn–Sham functional. This result appears to be quite general; when calculations were performed with a range of input charge densities the energy obtained from the Harris functional was always more accurate than the Kohn–Sham result. In each case the Kohn–Sham energy was an *overestimate* of the self-consistent result while the Harris result was an *underestimate*. Under these circumstances one can use the Kohn–Sham

and Harris functionals to give upper and lower bounds to the total energy, with the exact result being closer to the Harris energy. We have presented an explanation of this effect in terms of the long-wavelength instability encountered in solving the Kohn–Sham equations. This is a very important observation because techniques involving evaluation of the total energy using approximate charge densities are likely to be used when the system is large and it is for large systems that the long-wavelength instability is most pronounced. Therefore it seems that the Harris functional will be useful in total energy calculations whether or not the output charge density is available.

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