First principles systematics of ordered metallic monolayers: I. Groups I and II through Sr

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Abstract. Density functional calculations, in the local density approximation, are reported for hexagonal monolayers of Li, Be, Na, Mg, K, Ca, Rb and Sr. In parallel with the well known study of bulk metals by Moruzzi, Janak, and Williams, we calculate the equilibrium lattice parameter and the electronic properties at that configuration. Notable findings include the occurrence of both bond contraction and expansion, universal scaling of the equation of state, and densities of states at the Fermi level much larger than for bulk in Be and Sr. The possible existence and the characterisation of well localised surface states at Γ in Mg, Ca and Sr somewhat analogous to the state already found both experimentally and theoretically in Be are considered in detail.

1. Introduction

With this paper we begin a comprehensive theoretical investigation of the properties of the 31 elemental metallic monolayers with $Z < 50$. The treatment will focus on trends, hence will parallel and complement the well known systematic study of bulk metals by Moruzzi *et al* (1978; MJW hereafter).

Although unsupported n-layers ($n = 1, 2, 3, 4, \ldots <$ roughly 10 atomic planes) are not a laboratory commonplace, there are several strong reasons for studying them theoretically. First, there has been a great deal of effort recently to study low-n overlayers on diverse substrates. This interest is largely a result of development efforts for smaller, faster electronic devices, with practical electronic devices rapidly approaching the limiting overlayer, $n = 1$. An essential aspect of understanding monolayers on substrates is to distinguish their intrinsic properties from those resulting from interaction with the substrate. An experimental example (Onellion *et al* 1986, Dowben *et al* 1987) is Hg on Ag(100). This task requires independent knowledge of the properties of the unsupported 1-layer.

Second, the finite thickness of a film introduces a second scale length, in addition to the usual Fermi wavelength k_F, which should produce quantum size effects (Gersbacher and Woodruff 1971, Cooper 1973, Schulte 1976, Mola and Vicente 1986, Feibelman 1983, Feibelman and Hamann 1984, Ho and Bohnen 1985, Ciraci and Batra 1986, Craig and Garrison 1986, Batra *et al* 1986). The two length scales are sensitive, distinct functions of equilibrium lattice spacing. When one recalls that the one-electron proper-

ties even of simple bulk metals are sensitive functions of strain (Zittel *et al* 1985), and that, for the few 1-layers treated thus far (Wimmer 1983a, Boettger and Trickey 1984, 1986a, Batra 1985, Ciraci and Batra 1986), the predicted equilibrium lattice spacing differs quite significantly from calculated bulk values, it becomes clear that predicting quantum size effects in 1-layers must be done at their calculated equilibrium lattice parameters.

Third, we have demonstrated elsewhere (Boettger and Trickey 1986b) that it is possible to identify the precursor of a highly localised surface state among the electronic energy levels of a 1-layer. A systematic study of metal 1-layers may therefore yield predictions and/or verifications of such localised surface states.

Here we treat the equilibrium geometry and properties for 1-layers of Li, Be, Na, Mg, K, Ca, Rb and Sr. As in MJW, the calculations are in the local density approximation (LDA) to density functional theory (DFT; reviews and references to original literature are found in March and Lundqvist 1983, Dahl and Avery 1984, Callaway and March 1984, Langreth and Suhl 1984) in non-spin-polarised, non-relativistic form. Subsequent papers will treat the other elemental metallic 1-layers by periodic table grouping. So far as we are aware, the only directly relevant earlier work (other than ours: Boettger and Trickey 1984, 1986a) is Wimmer's (1983b, 1984) full-potential linearised APW treatment of 1-layers with unrelaxed (i.e., experimental bulk) lattice parameters.

Section 2 summarises the relevant methodological features, § 3 treats the calculated cohesive properties (lattice parameters, cohesive energies, equation of state, bulk moduli, etc.), while § 4 connects these results with work on universal equations of state. Kohn–Sham eigenvalues, densities of states, and possible surface states are presented in § 5, with brief concluding commentary in § 6.

2. Methods

We solve the Kohn–Sham (KS) LDA equations by use of a substantially refined version of the linear combination of gaussian-type orbitals, fitting-function (LCGTO FF) scheme of Mintmire *et al* (1982), itself an extensive development of the procedure introduced by Sambe and Felton (1975). The calculations are fully self-consistent, include all electrons, and make no shape approximations regarding the LDA potential. The procedure is more general than the muffin-tin KKR method used by MJW. Given the packing of most bulk metals, use of a muffin-tin potential surely introduces much smaller errors in those systems than it would were muffin-tinning to have been used in a 1-layer.

In outline, the LCGTO-FF procedure expands each KS orbital in a finite basis of hermite gaussian functions (hereafter, the 'KS basis'). The calculation of coulombic matrix elements is speeded and the requisite number of primitive integrals reduced by expanding the charge density $n(r)$ in a second basis of hermite gaussian functions (hereafter, the 'Q basis'). The charge expansion coefficients are determined by variational minimisation of the magnitude of the spurious coulomb energy introduced by charge fitting (Dunlap *et al* 1979). Multipolar summations are used to incorporate coulombic contributions from remote sites, with stringent numerical tests to insure proper convergence.

An additional auxiliary basis of hermite gaussians (the 'XC basis') is introduced to expand the two exchange-correlation functions which are non-linear in $n(r)$ that are required in LDA calculations. These are the energy kernel $\varepsilon_{XC}[n]$ and the exchange-correlation potential $V_{XC}[n]$. The XC expansion coefficients are determined by least-squares fit to $V_{XC}[n]$ and $\varepsilon_{XC}[n]$ generated from the fitted $n(r)$, using numerical inte-

gration to calculate the fitting matrix. Various constraints are built into the procedure, including that the density-weighted average of each of the fitted exchange–correlation functions be the same as that for the exact density (Dunlap *et al* 1979, Andzelm *et al* 1985). The fitted density is monitored to avoid any significant spurious negative electron density on the numerical integral grid.

In addition to the evident benefits of generality and flexibility afforded by this methodology, there are some potential vulnerabilities. The most obvious is selection of three interdependent basis sets. In previous work (Boettger and Trickey 1984, 1986a), we picked the KS basis from lists constructed for Hartree–Fock calculations, frequently with substantial modification from experience with crystalline LDA-LCGTO calculations and with testing, in the 1-layer, for approximate linear dependencies. Also in that work, the Q and XC bases were constructed according to 'Dunlap's rules' (Dunlap *et al* 1979). These fix each Q-basis orbital exponent as twice a KS basis exponent and each XC exponent as two-thirds of a KS exponent. The XC basis that results has the sometimes unfortunate property, of course, of being more diffuse than the KS basis, so even if the latter does not exhibit approximate linear dependencies, such an XC basis may behave quite nastily.

Here we used the Dunlap rule for the Q basis in Li, Be, Na and Mg, with the XC basis identical to the KS one. The KS bases for Li and Be are from van Duijneveldt (1971) with p bases from crystalline experience. The KS bases for Na and Mg are from the tabulation of Huzinaga *et al* (1971) (specifically the second 12s and the 7p part of the 11s7p) with an added p function between the most diffuse and next-most diffuse p function, and the most diffuse p function then deleted for p_x and p_y but retained for p_z. It is important in the Q basis to symmetrise the p^2 (i.e. d-like) contributions into fitting functions with pure cartesian d symmetry, so the Q basis must have the same number of p_x, p_y and p_z members. (The only d symmetry which is compatible with film symmetry is that which transforms as $z^2 - (x^2 + y^2)/2$.) Hence we applied Dunlap doubling to all the p_x and p_y functions and to all but the most diffuse p_z to generate the Q basis.

For K and Ca the KS bases are Wachter's (1970) bases enriched by an additional diffuse p_x and p_y, the two additional p_z, and a simple 5d. For Rb and Sr the KS bases are from Huzinaga (1977) with slight shifting of the outermost s functions, deletion of the tightest p, addition of one diffuse p_x and p_y, two additional diffuse p_z and a single diffuse d. Generation of the Q basis by straightforward application of Dunlap's rule however generates an s manifold which is a bit too heavy in compact functions and a d manifold which is far richer than needed. Therefore, for K, Ca, Rb and Sr, Q bases were manufactured by the following procedure. First, double the most diffuse s exponent in the KS basis (an application of Dunlap's rule). Then, temper inward (spatially) by a multiplicative factor of 2.4 to construct nine more s members of the Q basis, then temper by 3.00, 3.50, 4.50, and 6.00 to construct the remaining four s-type Q functions in K and Ca and also temper by 10.00 to gain one more tight s-type function for Rb and Sr. The d (= p^2) part of the Q manifold was constructed by doubling the most diffuse KS p exponent, then tempering inward by a factor of 3.00 to generate five more functions. For K, Rb, and Sr all used the same d-manifold for the Q basis; this would have been the case for Ca as well except that we had already completed the calculations for Ca when the idea arose. The XC basis was generated in all four cases by dividing each Q basis exponent by two, a kind of inverse Dunlap rule.

The bases which result range from (KS: 9s/5p; Q: 9s/4d; XC: 9s/4d) for Li to (KS: 17s/ $12p_{x,y}13p_z$; Q: 15s/6d; XC: 15s/6d) for Sr. For the sake of reproducibility, tabulations of all the bases are available on request from the authors.

The most suitable choice of LDA model is a matter of much discussion. The Wigner interpolation formula added to Xα with $\alpha = \frac{2}{3}$ seems to give superior work functions,

for example (Feibelman 1983, Feibelman and Hamann 1984). Unambiguous comparison with MJW, however, requires the use of the same LDA parametrisation. Thus we used the Hedin–Lundqvist (HL) model (see MJW for references and parameters).

By now it is well established that the bare KS eigenvalues are not rigorously interpretable as one-electron excitation energies (for references to this extensively studied problem consult Perdew 1986, Pickett 1986, Trickey 1986), except for the KS ε_F (Levy *et al* 1984, Ambladh and Von Barth 1985). We report them nevertheless, just as did MJW, and as is near-universal practice (Wilkins 1980). The justification is in part continuity with MJW and the rest of the vast energy band literature, and partly that practical experience supports what the theorem just cited (about the authenticity of the KS ε_F) would lead one to hope, namely, that the worst deficiencies of KS eigenvalues as physical energy bands are for insulators and semiconductors or for metallic states far from the Fermi level.

Simple coordination number arguments as well as test calculations argue persuasively for the system symmetry adopted here, hexagonal. (Wimmer 1983b also cited experimental evidence on overlayer formation in support of the same choice.) In terms of surface structure, this symmetry corresponds to BCC and FCC (111) or HCP (0001) faces. The calculations reported here utilised 19 points in the irreducible wedge of the two-dimensional BZ. All were converged to 0.01 mH iteration-to-iteration shift in total energy.

In keeping with our goal of complementing MJW's work, these calculations are non-relativistic. Wimmer's monolayer studies (1983b, 1984) treated the core electrons fully relativistically and the valence electrons scalar-relativistically (i.e., with neglect of spin–orbit interactions). When comparisons of our results with his are made it may be valuable to keep this difference in mind. A more important difference, especially for the light elements, is that his calculations were made at nearest-neighbour distances corresponding to crystalline values from experiment.

3. Cohesive properties

The calculated equilibrium nearest-neighbour spacing a_e and binding energy E_b are compared with the calculated bulk values from MJW in table 1 (where we have corrected the MJW calculated lattice spacing to its zero pressure by use of the bulk modulus which they calculated). Also compared there is E_b for monolayers at experimental bulk nearest-neighbour spacing as obtained by Wimmer (1983b, 1984). For the alkali metals, we have recalculated the cohesive energy given by Wimmer because he used the paramagnetic atom limit. On both physical grounds and for reasons of clarity of comparison with MJW, it is preferable to use the spin-polarised atom instead. Both spin-polarised and paramagnetic total energies for each atom were calculated with the same basis (the films basis enriched so that the $p_{x,y}$ basis was as extensive as the p_z basis). The paramagnetic atomic energies were calculated with the films code at $a = 50$ au in order to maintain algorithmic consistency, with spin-polarisation shifts calculated independently from a gaussian basis atom code (which does not employ fitting function techniques). The spin-polarisation shifts were added to the cohesive energy reported by Wimmer. In order that any other total energies be recoverable if desired, we report the paramagnetic and spin-polarised atomic total energies in table 2.

Table 1. Calculated equilibrium nearest-neighbour distance a_e (au) and binding energies E_b (eV) for 1-layers and bulk. Note that Wimmer's (1983b, 1984) values are at experimental crystalline lattice spacings (column labelled 'Expt'), not monolayer equilibrium.

	a_e (au)			E_b (eV)		
	1-layer (present)	Bulk[a] (MJW)	Expt	1-layer (present)	Bulk[a] (MJW)	1-layer (Wimmer)
Li	5.78	5.55	5.70	-1.11	-1.65	-1.01
Na	6.64	6.67	6.92	-0.81	-1.12	-0.74
K	8.28	8.30	8.55	-0.65	-0.90	-0.58
Rb	8.92	8.90	9.14	-0.61	-0.65	-0.52
Be	3.99	4.19	4.20	-3.27	-3.97	-2.94
Mg	5.68	5.94	6.04	-1.02	-1.69	-0.88
Ca	7.01	7.08	7.46	-1.31	-2.24	-1.17
Sr	7.91	7.69	8.13	-0.99	-1.89	-0.94

[a] MJW (1978) adjusted via calculated bulk modulus to $P = 0$ value.

Table 2. Atomic total energies and spin-polarisation shifts (Ryd).

Element	Paramagnet	Spin-polarised shift
Li	-14.680724	-0.027154
Na	-322.86070	-0.023536
K	-1196.3444	-0.019824
Rb	-5872.3431	-0.016728
Be	-28.90964	—
Mg	-398.25186	—
Ca	-1351.4281	—
Sr	-6258.5547	—

Typically E_b was calculated at six to eight values of a. The resulting curves are extremely well represented by a least-squares fit to the quadratic

$$E_b(a) \simeq E_b(a_e) + \tfrac{1}{2}\partial^2 E/\partial a^2|_{a_e}(a - a_e)^2. \tag{1}$$

Therefore, the curves can be regenerated by use of the second derivative values given in table 3 for the range of a given there.

From table 1 it is clear that Wimmer (1983b, 1984) found less binding than the present results. Only part of the difference can be traced to his use of experimental crystal lattice parameters, since all our binding energy curves lie below his at those lattice spacings. On the basis of K and Rb it would be tempting to attribute the remaining discrepancy to use of relativistic corrections, but the presence of a large percentage deviation for Be makes this notion implausible. The shifts with respect to our own prior Li and Be (Boettger and Trickey 1984, 1986a) results are small and reflect continuing refinement of the algorithms used. Note that Wimmer found Mg to be the least bound alkaline earth 1-layer and Rb the least bound alkali; we concur on Rb but find Sr slightly less bound than Mg.

Table 3. Second derivatives from quadratic fit to E_b, equation (1), RMS deviation of that fit, and range of nearest-neighbour distances over which it was obtained.

System	$\partial^2 E/\partial a^2\big|_{a_e}$ (Ryd au^{-2})	RMS deviation (Ryd)	Range of a_{nn} (au)
Li	0.03041	1.4×10^{-5}	5.60–5.95
Na	0.02559	7.4×10^{-6}	6.45–6.80
K	0.01216	1.0×10^{-5}	8.00–8.60
Rb	0.01176	4.0×10^{-5}	8.40–9.40
Be	0.19102	3.9×10^{-5}	3.85–4.15
Mg	0.07679	3.2×10^{-5}	5.50–5.85
Ca	0.04630	4.9×10^{-5}	6.70–7.30
Sr	0.03087	8.0×10^{-5}	7.40–8.40

A trend which is immediately noticeable from table 1 is the contraction of nearest-neighbour separation in the alkaline earth metals. The situation in the alkali metals is subtler. Previously we (Boettger and Trickey 1986a) argued that, relative to *experimental* bulk lattice parameters (extrapolated to $T = 0$ K for Li by a density argument from BCC to FCC), the HL 1-layer calculations exhibited bond contraction for both Li and Be. Wimmer (1983a) had earlier found the same behaviour for Cs. A more systematic comparison is with *calculated* bulk values. From that perspective, the present results make clear that the lattice parameters of alkali metal 1-layers are not *significantly* contracted (taking the Na and K shifts as inconsequential) but are either close or expanded relative to bulk. This difference in predictions, depending on whether experimental or calculated bulk a_{nn} are used, arises because of what has usually been considered to be a problem in the LDA itself. It is known that even in the same state (e.g., crystalline solid) the more refined the LDA model, the more contracted will be the a_{nn} it predicts (Jansen *et al* 1984, Boettger and Trickey 1985, Blaha and Schwarz 1987), with calculated values from most models being smaller than the measured one. Comparison, therefore of the calculated 1-layer lattice parameter with the measured bulk value is very likely to give a prediction of 1-layer bond contraction just because of this idiosyncracy of the LDA.

The comparison of 1-layer and bulk nearest-neighbour distance is also dependent on the problem of the proper crystal phase. In table 1 all the quoted alkali metal a_{nn}'s are MJW's values for the BCC phase, even though, for example, Li is close-packed (Boettger and Trickey 1985 and references therein) at $T = 0$ K. Rescaling the BCC a_{nn} to corresponding FCC values for the same density, while perhaps tempting, turns out to be of questionable validity. The evidence for this is from our previous LSDA study of Li (Boettger and Trickey 1985) in which we found an FCC $a_{nn} = 5.577$ au versus a BCC value of 5.473 au. That difference is two-thirds of what naive equidensity scaling would have predicted. Furthermore, MJW's result for the BCC a_{nn} is substantially larger than ours, perhaps as a consequence of the muffin-tin approximation they used. Under these circumstances, it seemed best to make the simplest comparison, hence the choice in table 1.

The experimental evidence on alkali metal 1-layer lattice parameters is also somewhat more tangled than might at first seem to be the case. Ignatiev and Fan (1986) have measured lattice parameters for 1-layers of Li, K, Cs, and Al on graphite. For the Li 1-layer, they report $a_{nn} = 3.3$ Å or 6.236 au 'about 6% larger than that for metallic Li'. This value is actually about 9% larger than any experimental bulk BCC Li a_{nn} of which

Table 4. $B\Omega_0$ for crystals (both calculated and experimental) compared $(a^2/8)(\partial^2 E/\partial a^2|_{\text{equilib}}$ calculated for monolayers.

	1-layer (present) $(a^2/8)(\partial^2 E/\partial a^2|_{\text{equilib}}$ (Ryd)	Experimental[a] $B\Omega_0$ (Ryd)	MJW[b] $B\Omega_0$ (Ryd)
Li	0.13	0.12	0.13
Na	0.14	0.13	0.14
K	0.11	0.12	0.12
Rb	0.12	0.12	0.11
Be	0.38	0.41	0.47
Mg	0.31	0.36	0.42
Ca	0.28	0.30	0.29
Sr	0.24	0.29	0.33

[a] Values of B are from following references. Li: Anderson and Swenson (1985); Na, K, Rb: Anderson and Swenson (1983); Be: value quoted by Chou *et al* (1984); Mg, Ca, Sr: values quoted by Kittel (1976). Values of Ω_0 are experimental data quoted by MJW (1978).
[b] MJW (1978).

we are aware. It is, however, 6.3% larger than the nearest-neighbour spacing that FCC Li would have at the same density. The result seems to support 1-layer bond expansion in Li, but the authors state that the Li data were ambiguous and could be interpreted as signalling the presence of Li_2C_2 rather than metallic 1-layer Li.

The K data of Ignatiev and Fan show an 8% *decrease* in 1-layer a_{nn} relative to the 'K–K distance in bulk BCC potassium'. They used the bulk nearest-neighbour distance as $a_{nn} = 4.62$ Å $= 8.73$ au; Donohue's tabulation (1982) gives 8.55 au. Relative to the 8.73 au (8.55 au) value for the bulk metal, our calculation shows a bond contraction of 5.2% (3.2%). However, this apparent confirmation of alkali metal bond contraction in 1-layers again is misleading, since it too is based on a comparison of the *calculated* 1-layer value with the *measured* bulk value. By comparison, the MJW calculation of the bulk bond length is contracted 2.9% relative to experiment. The *purely theoretical* prediction therefore is just what is shown in table 1: nearly negligible contraction of the K 1-layer compared to bulk. The contraction found by Ignatiev and Fan is about 3% relative to this prediction. Possible explanations include: (1) undetected difficulties in the theoretical prediction, (2) substrate interaction causing the 1-layers measured to differ from unsupported ones, and (3) undetected experimental difficulties. Without further measurements we cannot choose among these speculations.

Two trends which can be discerned from table 1 are that, except for the Li–Be pair, the ratio $E_{b,1\text{-layer}}/E_{b,\text{bulk}}$ is larger for the alkali metal than for the adjacent alkaline earth. The anomalous cohesive behaviour of Be has been noted before; we return to it shortly. Second, that cohesive energy ratio rises through the alkali series but falls through the alkaline earth series. Presumably this behaviour is associated with the approach by the alkali metals to free-electron-like behaviour, hence to some better correspondence with the electron–gas contributions in the LDA model.

4. Universal equation of state

On the basis of simple dimensional arguments, the product of the bulk modulus B and equilibrium unit cell volume Ω_0 should be proportional to $a_{nn}^2 \mathrm{d}^2 E/\mathrm{d}a^2$. In table 4 we

Table 5. Universal EOS scaling lengths L for 1-layers, bulk cohesion, and surface–surface bonding. 1-layer results from present calculations via equation (5), bulk and surface–surface values from Rose *et al* (1983). All values in au.

	L (1-layer)	L_{bulk}	$L_{surf-surf}$	L/L_B	L/L_{SS}
Li	1.638	1.039	1.946	1.5765	0.8417
Na	1.525	1.058	2.060	1.4414	0.7403
K	1.982	1.228	2.419	1.6140	0.8194
Rb	1.953	1.247	2.494	1.566	0.7831
Be	1.122	0.586	0.775	1.9147	1.4477
Mg	0.988	0.605	1.474	1.6331	0.6703
Ca	1.442	—	—	—	—
Sr	1.535	—	—	—	—

compare $B\Omega_0$ for the crystal with $(1/8)\, a_{nn}^2 d^2 E/da^2$ calculated from the 1-layer at equilibrium. The agreement is remarkable given the crudeness of the argument and leads us to consider more systematic scaling of the computed $E_b(a)$ curves. In particular, consider the elementary algebraic rescaling of the harmonic fit (1) into the form

$$E_b(a) \simeq E_b(a_e) E_h^*(a^*). \tag{2}$$

Here the scaled harmonic energy, dimensionless length, and scale length are respectively

$$E_h^*(a^*) = 1 + (a^*)^2/2 \tag{3}$$

$$a^* = (a - a_e)/L \tag{4}$$

$$L = [E_b(a_e)/(\partial^2 E/\partial a^2)|_{a_e}]^{1/2}. \tag{5}$$

Precisely this sort of universal scaling of metallic equations of state (EOS), metal–metal adhesion, etc, has been studied in detail by Rose and co-workers (Rose *et al* 1981, 1983, 1984, Smith *et al* 1982, Ferrante *et al* 1983, Guinea *et al* 1984, Vinet *et al* 1986) and others (Spanjaard and Desjonqueres 1984), albeit not in the context of a harmonic universal energy, E^*. Modern exploration of such scaling seems to have begun with MJW. Recently Dodson (1987) has found a two-parameter scaling of bulk modulus with system density which holds for a remarkable range of metal crystals and alloys, semiconductors, and insulators and which relates reasonably well to a harmonic model.

An important connection to universal scaling is the length scale (5), which is identical with that adopted by Rose *et al* (1983) on other grounds. In table 5 we report the scale lengths L which result from our calculations and compare with their results for L_{bulk} and $L_{surface}$ when available. For the alkalis as well as Mg, we find systematic comparison, namely L/L_{bulk} approximately 1.5 ± 0.1 and $L/L_{surface}$ approximately 0.75 ± 0.1 (no comparison data are available for Ca and Sr).

The exception to this pattern is Be, with $L/L_{bulk} = 1.9147$ and $L/L_{surface} = 1.4477$. This result parallels the Be length scale behaviour found by Rose *et al* (1983), who characterised Be as 'completely anomalous'. They noted that for most metals the ratio $L_{bulk}/L_{surface}$ was, within 10%, 0.48, *except* for Be at 0.76. Clearly this scale length behaviour is another manifestation of the peculiar cohesive behaviour of Be (noted above) in going from bulk to 1-layer.
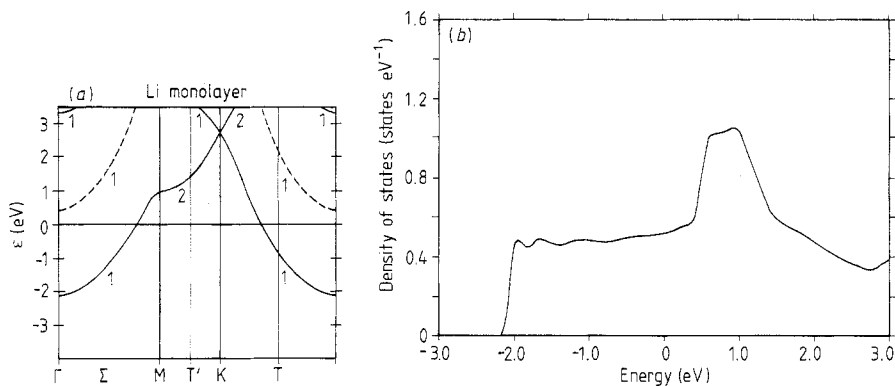
Figure 1. (*a*) Kohn–Sham eigenvalues (eV) and (*b*) Kohn–Sham density of states (states eV^{-1}/atom) for hexagonal Li 1-layer. In (*a*) symmetries with respect to the film plane are even (odd) for full (broken) curves.

Table 6. Calculated 1-layer and bulk work functions W (eV) and DOS at the Fermi level (states eV^{-1}).

| | W (1-layer) | W (bulk)[a] | DOS at ε_F | | |
			1L (present)	1L (Wimmer)	Bulk[b]
Li	3.58	2.90	0.52	0.56	0.48
Na	3.16	2.75	0.44	0.55	0.45
K	2.67	2.30	0.68	0.80	0.73
Rb	2.55	2.16	0.73	0.87	0.90
Be	5.39	5.10	0.34	0.35	0.054
Mg	3.99	3.66	0.60	0.57	0.45
Ca	3.15	2.87	1.53	2.14	1.56
Sr	2.92	2.59	1.31	2.32	0.31

[a] Be: Green and Bauer (1978); all others: Michaelson (1977).
[b] MJW (1978).

Rose *et al* (1981) obtained an analytic form for $E^*(a^*)$ by fitting to calculated bulk metal and metal–metal interface binding energy curves. In our notation the fit is

$$E^*(a^*) = (1 + 0.9a^*) \exp(-0.9a^*). \tag{6}$$

It is intriguing to note that, even though obtained in an entirely different context, this form fits our calculated Li 1-layer results with an RMS deviation of 4×10^{-4} eV over the range 5.6–5.95 au when L from table 5 is used.

5. One-electron properties

The energy bands (bare Kohn–Sham eigenvalues) and associated densities of states (DOS) are presented in figures 1–8, while the DOS at ε_F and work functions ($W = -\varepsilon_F$) are found in table 6.
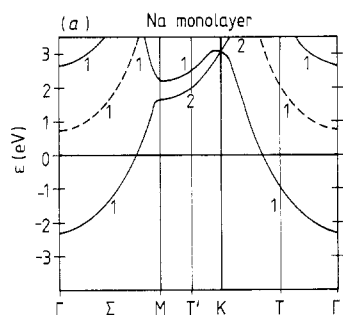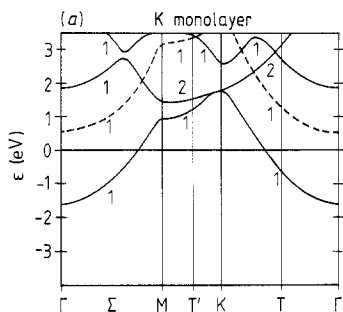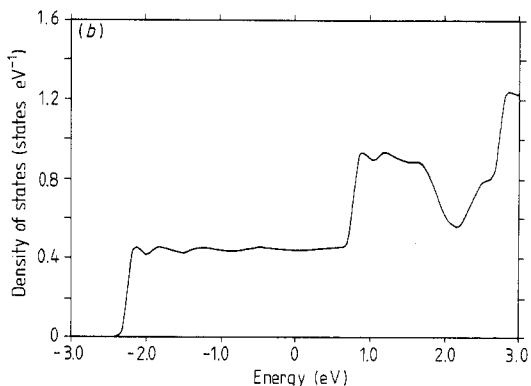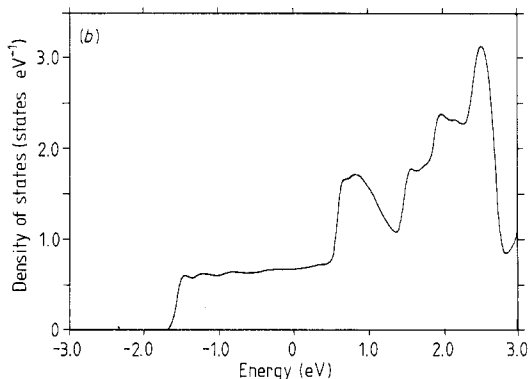
Figure 2. As in figure 1 for Na.

Figure 3. As in figure 1 for K.

Qualitatively the alkali metal bands and DOSs are not strikingly different, for the most part, from those of Wimmer (1983b, 1984). We do not find the low, rounded peak he finds at the bottom of every one of his DOSs but a pair of smaller bumps instead. This difference is solely a consequence of differing numerical techniques for BZ integration. Neither feature is physical, as can be seen by the nearly perfectly parabolic s bands at low energy found both by us and by Wimmer. For the two-dimensional BZ, such bands imply a low-energy DOS proportional to a step function; various bumps and peaks in the computed DOS reflect the ability or inability of a numerical technique to reproduce that step.

Systematic comparison of calculated DOSs is possible both for bulk from MJW and from Papaconstantopoulos (1986) and for 1-layers with Wimmer (1983b, 1984). For Li, the two crystal calculations are very much alike with a sharp peak at about 0.5 eV (all energies with respect to ε_F) and another (in Papaconstantopoulos' results) at about 2.5 eV. We find very free-electron-like behaviour below ε_F with a well defined peak about 0.6 eV wide beginning at 0.4 eV; Wimmer finds essentially the same thing except that the high-energy shoulder of the positive energy peak is much less well defined. For Na the two bulk calculations are essentially identical, as are the two monolayer calculations, except that the first positive energy peak is calculated by Wimmer to lie
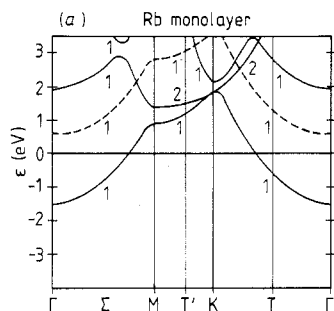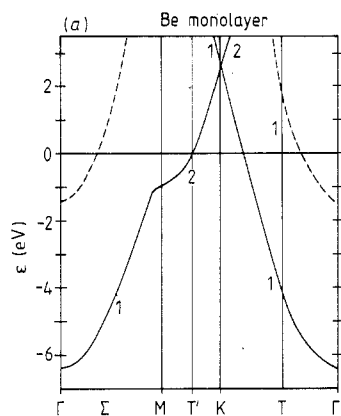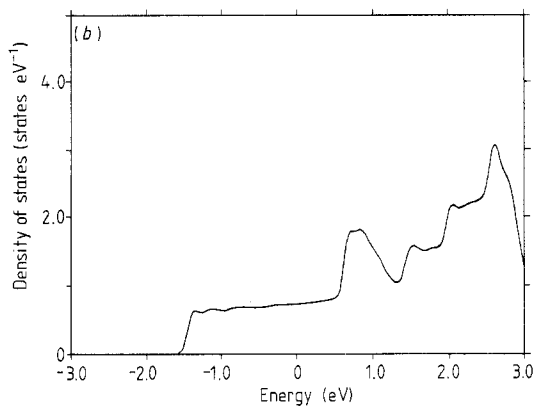
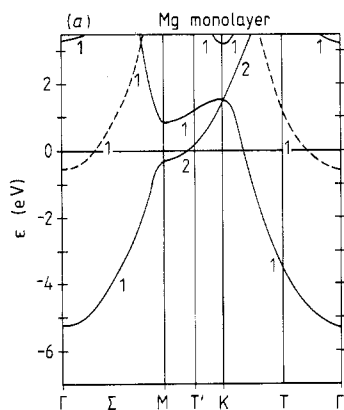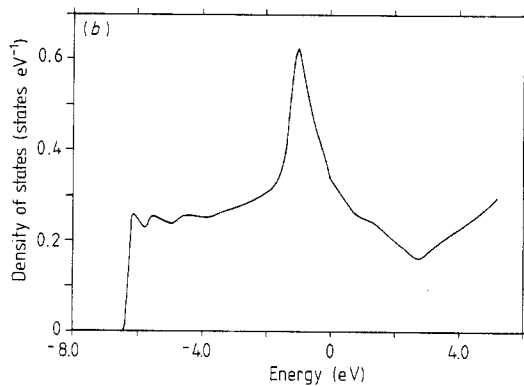**Figure 4.** As in figure 1 for Rb.

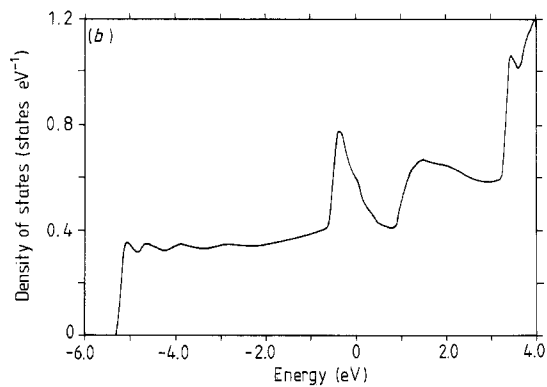

Figure 5. As in figure 1 for Be.

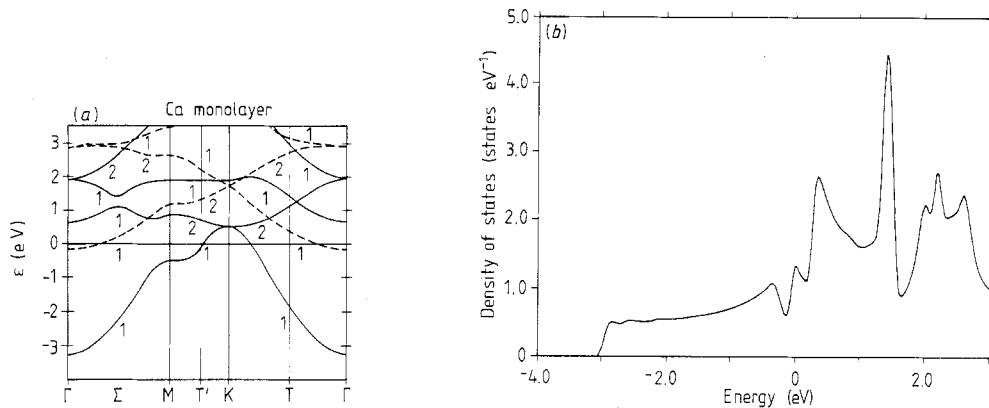
Figure 6. As in figure 1 for Mg.
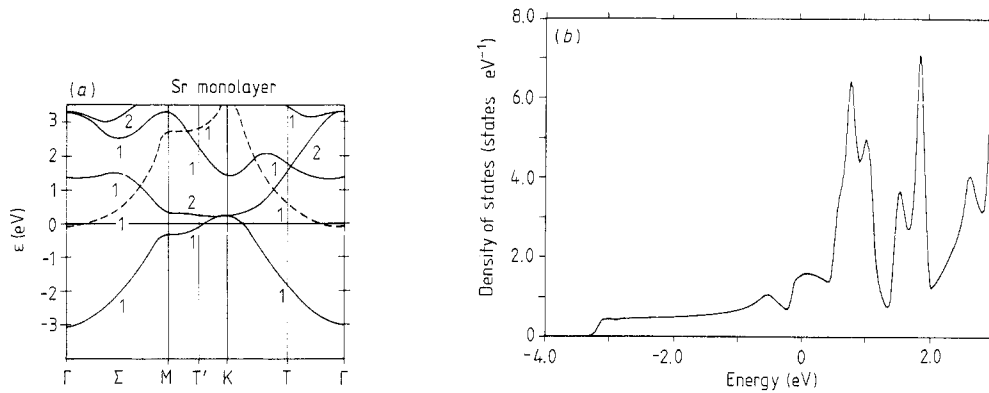
Figure 7. As in figure 1 for Ca.

Figure 8. As in figure 1 for Sr.

slightly lower and be slightly narrower than we find it. In K, MJW find substantially more structure in the first two volts above ε_F than does Papaconstantopoulos. This detail corresponds decently with that found in both 1-layer calculations, though we find a peak over 0.7–1.0 eV with much more definition than the corresponding object in Wimmer's results. The bulk Rb results agree that there is a sharp peak at about 0.2 eV and another of much higher amplitude at about 1.2 eV. Corresponding features occur in our 1-layer DOS, but shifted upward in energy by roughly one volt; Wimmer gets most of the same structure (one shoulder does not appear) over an energy range that is approximately a volt smaller.

For all the alkali metals we determine $N(\varepsilon_F)$ which are both smaller than Wimmer's and vary less with Z. The differences are as large as 20% (Na), hence should be discernible. MJW and Papaconstantopoulos agree on crystalline $N(\varepsilon_F)$ values to within 10% at worst (Na). The general agreement between our monolayer results and the two bulk calculations is no worse than that, except for Rb, where we find a 1-layer value 20% smaller than bulk. It would be nice to attribute this shift to relativistic versus non-relativistic calculations, but the attribution fails since the two bulk results are virtually identical.

Turning to the alkaline earths, we recall that study (Boettger and Trickey 1986b) of KS eigenvalues in Be n-layers ($n = 1, 2, 3$) provided unequivocal identification of the monolayer state at Γ of odd symmetry with respect to the plane which is 1.4 eV below ε_F (note figure 5) as the precursor of the highly localised state seen in clean Be surfaces by angle-resolved photo-emission. An important characteristic in that identification is that the state has no counterpart in the bulk crystalline bands. In this sequence of monolayers, we have seemingly similar states at Γ for Mg (at -0.55 eV with respect to ε_F), Ca (at -0.15 eV with respect to ε_F), and Sr (at -0.07 eV with respect to ε_F). They are not computational artifacts, since Wimmer finds them as well. None has a counterpart in the bulk bands of MJW, but this comparison is inconclusive, since differences in space group symmetries intrude.

There are angle-resolved photo-emission data (Karlsson *et al* 1982, Bartynski *et al* 1986) for a surface state on the (0001) surface of Mg, but it is only 0.1 eV above the projected bulk bands (at -1.6 eV) and, unlike Be, lies below another set of projected bulk bands. Without 2- and 3-layer calculations, it is difficult to conclude that the weakly bound state at Γ in the Mg 1-layer is anything other than the precursor of the Γ_{3+} bulk state (cf Papaconstantopoulos 1986, p59). This conclusion seems to be reinforced by study of the six- and ten-layer periodically repeated slab results of Chulkov and Silkin (1986), though they did not display their one-electron energies in detail.

There are also photoemission data (Ley *et al* 1981) for a (111) Ca surface state of -0.6 eV at Γ and correspondingly at -0.5 eV for Sr. Those same authors also did slab calculations (7-layers, periodically repeated, local density, pseudopotential) which produced a surface state in good agreement with experiment. The way in which the state evolved with the number of layers was not addressed, however. Comparison of their DOS calculations with ours might suggest that we have identified this state as well, but even cursory examination of the Ca 1-layer bands is enough to convince one that the 1-layer DOS peak at about -0.5 eV arises from the occupied bulk-like state at M.

What is not clear from either the 1-layer bands or the DOS for Ca and Sr is whether the weakly bound states at Γ are surface or bulk state precursors. It may be that they signal the existence of highly localised surface states in the heavier alkaline earths, somewhat analogous with the Γ surface state in Be, but the identification is not compelling. (The fact that they lie too close to ε_F compared with experiment is not a prohibitive barrier to this interpretation, since highly localised states are pushed up in energy artificially in LDA calculations by spurious self-interaction; Boettger and Trickey 1986b). Further study, on few-layer films and on slabs, will be needed to resolve the matter. In any event, the effective masses for these monolayer states will be quite large and rise substantially with increasing Z, since the bands in question flatten dramatically with Z.

Direct comparison of 1-layer and bulk DOSs for the alkaline earths shows some notable distinctions. The bulk Be DOS, according to MJW, has sharp peaks near -5.0 and $+0.5$ eV. Papaconstantopoulos finds the same two peaks at -3.1 and $+1.6$ eV; the difference is almost surely due to MJW's use of FCC symmetry as opposed to Papaconstantopoulos' use of the (correct) HCP lattice. The Be 1-layer has only one sharp peak below ε_F at -1.0 eV; Wimmer gets a broader version of this feature at about -0.7 eV. The most remarkable difference is a factor of five or more increase in the Be 1-layer $N(\varepsilon_F)$ as compared with the bulk result: 1-layer Be is a better metal than its bulk counterpart.

For bulk Mg, MJW find free-electron behaviour from the bottom of the DOS up to about -2 eV, where a small, sharp peak occurs followed by another just below the Fermi

level. In contrast, Papaconstantopoulos finds a rather ragged DOS below ε_F with a sharp peak around -0.6 eV. Again, the difference surely involves FCC (MJW) versus the actual HCP (Papaconstantopoulos) symmetry. Our 1-layer result is quite free-electron-like up to about -0.3 eV, where a sharp peak of substantial amplitude occurs. A pronounced shoulder occurs at about $+0.9$ eV. Wimmer does not find that feature. The 1-layer calculations agree in predicting a larger $N(\varepsilon_F)$ than for bulk (for which the two calculated values agree equally well).

In a similar vein, our Ca DOS has narrow peaks and steep valleys upward from about $+0.5$ eV, while Wimmer's are mostly broader and shallower. Here the bulk calculations differ noticeably, with MJW finding a shoulder and then a sharp spike centred barely below ε_F, while Papaconstantopoulos obtains a spike centred on ε_F preceded by a slight flattening in the DOS. The result is a quite different value for the crystalline $N(\varepsilon_F)$: 1.56 states eV^{-1} (MJW) versus 1.26 states eV^{-1} (Papaconstantopoulos). This difference may arise from non-relativistic versus scalar-relativistic treatments, although at $Z = 20$ it seems a bit unlikely. Superficially, the same problem appears to occur for the 1-layer values of $N(\varepsilon_F)$: 1.53 states eV^{-1} (present) versus 2.14 states eV^{-1} (Wimmer). Inspection of Wimmer's DOS plot however, shows clearly a value of about 1.4 states eV^{-1}. Though his plotted DOS is gaussian-broadened, we surmise that his tabulated value of $N(\varepsilon_F)$ is from the unbroadened DOS.

The same problem occurs for Sr. We get $N(\varepsilon_F) = 1.31$ states eV^{-1} as contrasted with Wimmer's tabulated value of 2.32 states eV^{-1} but a plotted value of about 1.5–1.6 states eV^{-1}, in much better agreement with our result. Both are much higher than MJW's bulk value of 0.31 states eV^{-1}. Papaconstantopoulos reports and plots $N(\varepsilon_F) = 0.0$ states eV^{-1} for Sr. Examination of his band structure diagram shows clearly that there are states of finite (indeed, small) slope at ε_F, so the reported null value of $N(\varepsilon_F)$ has to be an artifact of BZ sampling in his DOS calculation. We find a DOS peak at about -0.5 eV, another at ε_F, followed by two large-amplitude peaks in the next 1.5 V. Wimmer finds roughly the same features but with rather different amplitude ratios.

Our present calculations of W differ by little from what we previously reported (Boettger and Trickey 1984, 1986a) for Li but by 0.6 eV (about 11%) for Be. The Be shift from the previous value is primarily due to basis-set enrichment and secondarily to algorithmic refinements. For the alkali metals, our results and Wimmer's agree quite satisfactorily. Both exceed experimental bulk values by significant amounts (0.4–0.7 eV). The concord of Wimmer's results with these is not quite so good for the alkaline earths, though only Be is at all striking. We discussed this aspect of Be 1-layer behaviour previously and have nothing to add here. As with the alkalis, calculated W's exceed the experimental bulk values by about 0.3 eV across the series. Whether this is a bulk to 1-layer shift or a deficiency from comparing KS eigenvalues with experimental bulk W values is unclear.

6. Comments

Several conclusions come out of this study. First, the claim that theory predicts bond contraction of metal 1-layers relative to bulk crystals cannot so far be sustained unambiguously. A systematic prediction must avoid the known problem of lattice contraction in LDA relative to experimental values. Here we have avoided that problem by comparison solely of calculated values. Contrary to the bond contraction hypothesis (and some experimental data on overlayers) we predict bond expansion for Li, negligible

contraction for the other alkali metals, modest contraction for the lighter alkaline earths, and weak expansion for Sr. Very careful, unambiguous experimental assessment is needed to help resolve the matter.

Second, the calculated equations of state very clearly exhibit universal behaviour. This result is not entirely surprising if one reflects on the universal energy functional that is the heart of Hohenberg–Kohn theorem. Experimental verification that universal EOS scaling is valid for 1-layers (in addition to its known validity for bulk metallic cohesion, metal–metal interfaces, etc.) would be most interesting.

Third, we suggest that well localised surface states at Γ may exist in Mg, Ca and Sr, somewhat analogously with Be, but that the identification cannot be made with certainty on the basis of monolayer results alone. For Be and Sr we predict much higher 1-layer values of $N(\varepsilon_F)$ than found in the crystal. We also find work functions for all eight 1-layers which are substantially larger than experimental values reported for their bulk metallic counterparts. Experimental testing of these predictions would be very helpful in extending our understanding both of DFT in the LDA and intrinsic 1-layer properties.

Succeeding papers in this series will treat monolayers of the remaining metals in MJW by their groupings from the periodic table.

Acknowledgments

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