

## *Ab initio* pseudopotentials for orbital-free density functionals

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**Abstract.** – A method for producing pseudopotentials from first principles for use with orbital-free density functionals is presented. In several metallic systems, the orbital-free approach reproduces the results of Kohn-Sham calculations with non-local pseudopotentials with considerably less computational effort.

There has been a revitalization of interest in the use of orbital-free density functionals for electronic structure calculations [1]-[3], following the realization that extremely efficient *ab initio* molecular-dynamics methods, which scale almost linearly with system size, can be constructed in this way [4]-[9]. At the same time, there has been continued interest in finding functionals with which to represent the electron density at the metal/vacuum interface [10].

The central problem, in substituting an orbital-free (O-F) approach for the usual Kohn-Sham (K-S) realization of density functional theory [11], is to find a representation of the kinetic energy. It has been shown how functionals which replicate the behaviour of the K-S functional in simple metallic systems, such as Na and Al [12], may be constructed using the linear [2], [3], [5], [10] and quadratic [3], [12] response functions of non-interacting electron gas, together with the classical Thomas-Fermi and von Weiszäcker functionals [1].

Solving the kinetic-energy problem does not, however, mean that full, *first-principles* O-F calculations on metals are immediately possible. The orbitals play a second role in *ab initio* K-S calculations, which is to allow a representation of non-locality in the pseudopotentials which are used in practical calculations where plane-wave basis sets are employed. Such pseudopotentials are constructed from all-electron calculations on the isolated atom [13]. Different potentials are required for atomic orbitals of each angular momentum and these are implemented in the condensed phase calculations by projecting out of the *orbital wave functions* the *s*, *p*, etc. components around each atom and applying the appropriate pseudopotential to each. In the O-F calculations, the wave functions are not represented, only the total density. Hence, *local*

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pseudopotentials have been used, *i.e.* the valence electron-ion interaction has been written

$$E_{\text{ext}}[\rho] = \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}), \quad (1)$$

where  $\rho(\mathbf{r})$  is the valence density at the point  $\mathbf{r}$ , and  $V_{\text{ext}}$  is the electron-ion interaction potential

$$V_{\text{ext}}(\mathbf{r}) = \int d\mathbf{r}' v_{\text{ps}}(|\mathbf{r} - \mathbf{r}'|) \sum_i \delta(\mathbf{r}' - \mathbf{R}^i) = \int d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{r}} S(\mathbf{k}) v_{\text{ps}}(k). \quad (2)$$

In the latter  $\mathbf{R}^i$  is the position of ion  $i$  and  $S(\mathbf{k})$  is the ‘‘structure factor’’ ( $\sum_i e^{i\mathbf{k}\cdot\mathbf{R}^i}$ ).

In the O-F calculations done to date, *empirical* local K-S pseudopotentials [14], [15] have been used. In this paper we take up the issue of how to construct suitable pseudopotentials for use in O-F calculations from *first principles*, on the basis of K-S all-electron calculations on atoms, thereby expanding the range of systems for which suitable pseudopotentials are available.

The most obvious way to obtain a local potential from an *ab initio* pseudopotential would be simply to use one angular momentum component of the latter. For an alkali element, for example, it might be imagined that the  $s$  component would suffice but, in K-S (and O-F) calculations, such potentials give very poor bulk properties (see, *e.g.*, [16]). This is not a deficiency of the local representation *per se*; for sodium the empirical, local Topp-Hopfield [14] potential gives an excellent account of the solid and liquid states [5], [17].

An alternative is to perform K-S calculations, with an *ab initio* non-local potential, on some representative bulk state, and then to construct a pseudopotential by requiring that an O-F calculation, with this potential, reproduce the K-S bulk state electron density and energy. Similar methods have been proposed previously to construct effective pair potentials [18] within the context of linear-response theory. If, for a periodic system,  $\rho_{\text{K-S}}(\mathbf{k})$  is a Fourier coefficient of the K-S density, then we require that the orbital-free functional be stationary when evaluated with this density with the to-be-determined local pseudopotential, *i.e.*

$$\frac{\delta T_e}{\delta \rho(\mathbf{k})}[\rho_{\text{K-S}}] + \frac{\delta E_{ee}}{\delta \rho(\mathbf{k})}[\rho_{\text{K-S}}] + \frac{\delta E_{\text{ext}}}{\delta \rho(\mathbf{k})}[\rho_{\text{K-S}}] = F(\mathbf{k})[\rho_{\text{K-S}}] + V_{\text{ext}}(\mathbf{k}) = 0. \quad (3)$$

Here  $T_e$  and  $E_{ee}$  are the kinetic energy and electron-electron interaction (Hartree, exchange and correlation) functionals. Equation (3) therefore gives a simple linear relationship between  $V_{\text{ext}}(\mathbf{k})$  and  $F(\mathbf{k})[\rho_{\text{K-S}}]$  and, if the reference bulk state is of sufficiently high symmetry, the local pseudopotential  $v_{\text{ps}}(k)$  may be obtained by averaging  $V_{\text{ext}}(\mathbf{k})/S(\mathbf{k})$  over the  $\mathbf{k}$  vectors with equal lengths. We note that this procedure is generally applicable and not restricted to linear response; it may be generalized for the use of non-linear core corrected pseudopotentials [19].

We have used a crystal at the experimental density as the bulk reference state. Other choices are possible, notably a single atom embedded in an electron gas background [18]. The use of the crystal has the disadvantage that the Fourier coefficients of the density are non-zero only at the Bragg vectors of the reciprocal lattice, which become sparse at low  $k$ . To circumvent this difficulty, an analytic (gaussian  $Ae^{-bk^2}$ ) form for the pseudopotential is assumed at low  $k$ . The parameters are fixed by matching with  $v_{\text{ps}}(k)$  at the lowest Bragg vector and requiring agreement of the total O-F energy with the total K-S energy for the crystal. In the cases studied, the single Gaussian described the shape of the potential well over the first three non-zero  $k$  values. At higher values of  $k$ , values of the pseudopotential are obtained by interpolation.

We have used the Troullier-Martins (T-M) procedure [20] to generate *ab initio* pseudopotentials. The cut-off radius was taken to be 90% of the radius of the outermost maximum in the valence orbital density. The CASTEP program [21] was used to effect the K-S calculations on

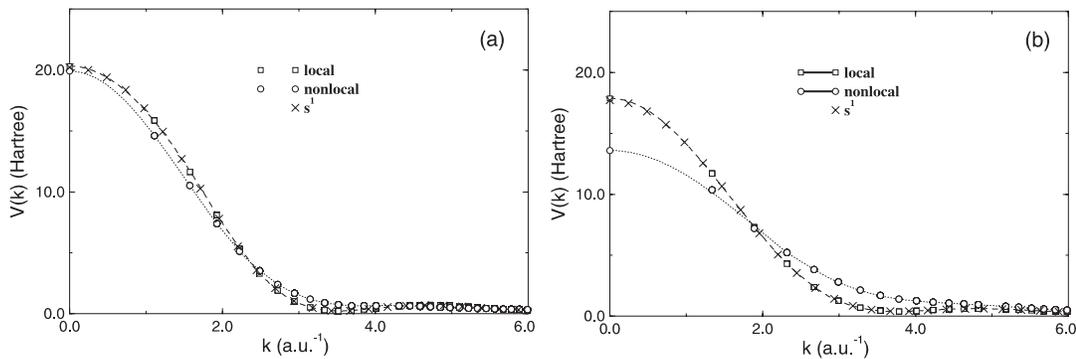


Fig. 1. – The non-Coulombic parts of the O-F pseudopotentials for sodium (a) and lithium (b) in reciprocal space as generated from local (squares) and non-local (circles) *ab initio* pseudopotentials are compared. The crosses mark the values of the original local *ab initio* potential, which coincide closely with the O-F potential obtained from it. The lines are functions fitted to the discrete potential values which emerge from the inversion procedure.

the crystal. The LDA functional [22], [23] was used for the electron-electron interactions in both K-S and O-F calculations. Allowing for gradient-corrected functionals would be straightforward. However, theoretical studies [24] of nearly free electron systems show that the LDA gives the correct form for the screening functional, whilst the gradient-corrected functionals give an incorrect wave vector dependence, so retaining the LDA for metals is preferable. In the K-S calculations we have used simple cubic periodic boundary conditions, so that the bcc unit cell contains two atoms, and performed very extensive Brillouin-zone sampling (10-20 sets of Monkhorst-Pack points [25]) with the full crystal symmetry imposed on the B-Z sampling points used. Very large cut-offs were used, to ensure complete convergence in the representation of the potentials and wave function. The O-F calculations have been done with the  $T_{\frac{5}{6}, \frac{5}{9}}$  kinetic-energy functional, described in ref. [12].

Calculations were first performed for Na and Li with a local *ab initio* potential, obtained from the T-M program for the  $s^1$  atomic configuration. In fig. 1 the O-F local pseudopotentials obtained *via* the inversion procedure outlined above (squares) are compared with the initial local *ab initio* potentials used in the K-S calculations (crosses). It can be seen that the agreement between the two potentials is excellent, within the convergence and interpolation precision ( $\sim 0.1\%$ ), showing that the O-F functional is reproducing the K-S behaviour and that the inversion process is functioning correctly.

Figure 2 shows cohesive energies *versus* cell volume for K-S and O-F calculations with the local potentials described above. These show that the O-F calculations reproduce the K-S results closely, as seen previously [12]. They also show that the *ab initio* local potentials (and therefore the O-F potentials obtained from them) give a poor representation of the electron-ion interactions in the bulk, giving significant errors in the predicted cohesive energy and equilibrium lattice parameter. The cohesive energies are obtained from the difference between the bulk energies per atom and the isolated atom energies (with the same pseudopotentials). The latter have been corrected for electron self-interactions [23], [26] — a procedure which systematically improves calculated cohesive energies of metals, by  $\sim 0.2$  eV for Na and Li.

Non-local *ab initio* potentials were generated with the T-M scheme using an  $s^1p^0$  atomic configuration. The local, O-F pseudopotentials which result from the inversion procedure with this potential for Na are illustrated in fig. 1 (a). It is not very different from that generated with the local *ab initio* starting point, confirming that the non-locality effects are not very large

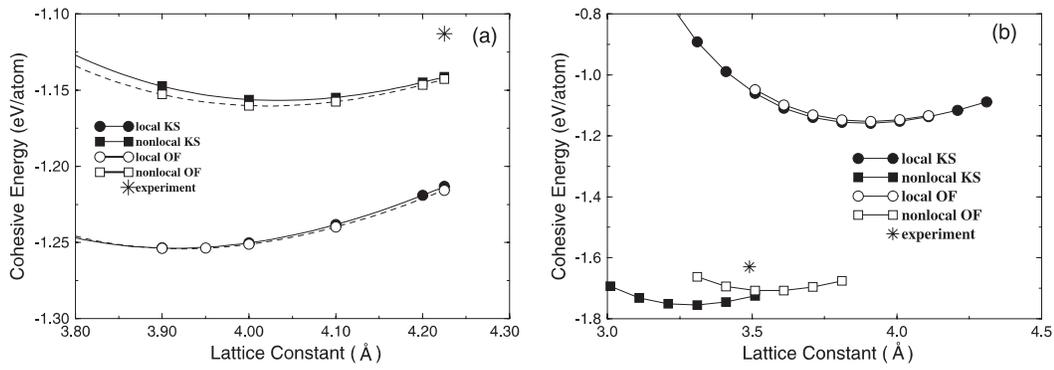


Fig. 2. – Cohesive energies *vs.* lattice parameter obtained in O-F and K-S calculations for sodium (a) and lithium (b) with the pseudopotentials described in the text compared with the experimental cohesive energy and lattice constant (asterisk).

in sodium. Figure 2 (a) contains cohesive energies *vs.* cell volume results from the K-S and and O-F calculations. These show a close agreement with each other, which demonstrates that for sodium much of the effect of the non-locality in the *ab initio* potential may be recaptured by using a local function (as also witnessed by the success of empirical local potentials for this element [14]). Agreement with the experimental data for the cohesive energy and lattice parameter is also good, at the level achieved in state-of-art K-S calculations [16].

In Li, it is to be expected that the non-locality effects will be more severe than for Na: the  $2s$  and  $2p$  are of similar size and energy and may be expected to hybridize more efficiently than the  $s$  and  $p$  orbitals in the other alkalis. This is confirmed by the large difference between the local-generated and non-local-generated O-F pseudopotentials in fig. 1 (b). The O-F results do not fully recapture the K-S results for the cohesive energy *vs.* volume (fig. 2 (b)). However, both

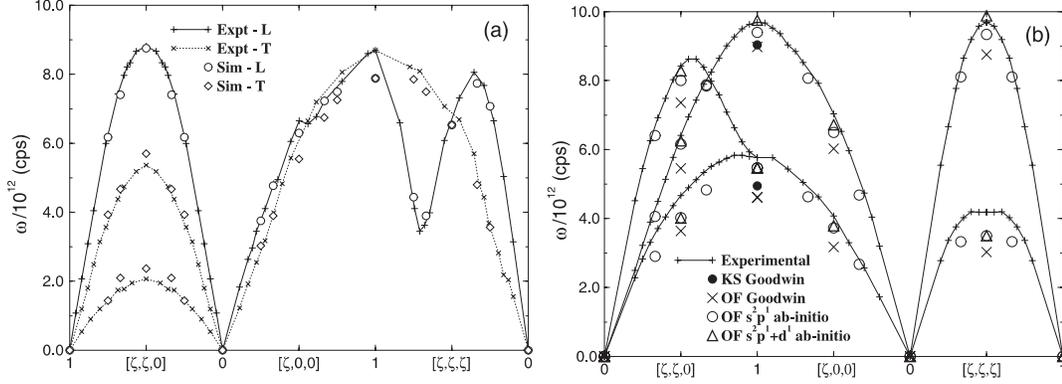


Fig. 3. – Phonon dispersion curves for <sup>7</sup>Li (a) and for Al (b) at 293 K, obtained with the derived pseudopotentials in the O-F calculations, are compared with experiment [27] and [29]. In (a) the Li pseudopotential is derived from the non-local *ab initio* potential, as described explicitly in the text. In (b) results are compared for the empirical Goodwin [15] potential (for which some K-S results are also shown) and for O-F potentials derived from *ab initio* potentials with  $s$  and  $p$  and  $s$ ,  $p$  and  $d$  non-locality.

give an equilibrium lattice parameter and cohesive energy which is in much better agreement with experiment than obtained with the *ab initio* local potential. By chance, the O-F result for the equilibrium geometry is better than the K-S! This shows that the full effects of the non-locality are not being recaptured in the O-F potential. However, the potential which is obtained is providing an acceptable representation of the cohesive energy and lattice parameter of the lithium crystal.

Given that the O-F potential has been generated for the bcc crystalline environment, it is important to test its predictions against experiment for other, less symmetrical configurations. To this end, the phonon dispersion relations for Li along the principal symmetry directions have been calculated by performing molecular dynamics with the O-F code at a temperature of 293 K and at the zero pressure density predicted by the potential. The phonon frequencies are calculated from the spectra of appropriate current correlation functions, as described in detail in ref. [12]. The results are compared with experiment [27] in fig. 3. In general the agreement is excellent; significant (5%) disagreements are only in evidence for two of the transverse branches. Good agreement is also found with the high-quality K-S, frozen-phonon calculations on Li reported in fig. 1 of ref. [28], where a non-local *ab initio* pseudopotential very similar to ours was used (our data and that of [28] are both compared to the same experimental results).

Also in fig. 3 we report results, obtained as above, on the phonon dispersion in aluminium. We had previously studied Al [12] with the empirical Goodwin potential [15], finding good agreement between the O-F and K-S calculations at the [100] zone boundary. New results are also shown in fig. 3(b) for local O-F pseudopotentials generated by the present procedure from two non-local T-M potentials which contain *s* and *p* and *s*, *p* and *d* components, respectively. The new potentials systematically improve upon the Goodwin potential bringing the calculated phonons into quite good agreement with experiment [29]. Furthermore, the degree of improvement increases with the degree of non-locality in the parent pseudopotential.

A further test of transferability is to examine the relative stability of other crystal structures with the same pseudopotential. Experimentally [30] Li and Na (but not the heavier alkalis) undergo a low-temperature martensitic phase transition from bcc (the high-temperature phase) to a close-packed structure. The O-F calculations are in full agreement with these observations. With pseudopotentials generated using the bcc crystal as the reference state, the energy minima of the close-packed structures (hcp and fcc) of Li and Na are found to be very similar and to be lower than the bcc structure (by 0.05 and 0.006 mHartree, respectively). Potassium, on the other hand, is predicted to have bcc as the lowest-energy phase. The energy differences are in good agreement with the estimates of the vibrational contribution to the free-energy differences between bcc and the close-packed phases at the transition temperatures [30]. The transition volumes are also in good agreement with experiment.

In conclusion, we have described a method for producing local potentials, ideal for orbital-free density functionals, which include some element of the non-locality of *ab initio* pseudopotentials. Results of similar quality have been obtained for other metals in groups 1, 2 and 13. The methods are being used in large-scale simulations of defective solids and liquids, both of the pure metals and their alloys.

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