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## LETTER TO THE EDITOR

# Non-singular atomic pseudopotentials for solid state applications

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**Abstract.** A method for obtaining non-singular pseudopotentials from self-consistent atomic calculations is presented. Outside the core region the nodeless radial pseudo-valence wavefunction is taken to be identical to the real wavefunction and inside it is represented by a smooth analytical function. Both the first and the second derivatives of the radial pseudo-wavefunction are matched to the *ab initio* result at a core radius which depends on angular momentum. The resulting non-local self-consistent core pseudopotential is energy independent over a wide energy range. It is smooth and non-singular and is suitable for solid state bandstructure methods which make use of plane wave basis set expansions. This approach is so simple that it can be mostly carried out analytically, in contrast to a recently proposed method in which a pseudopotential is obtained by modifying the atomic potential instead of the wavefunction.

Recently Hamann *et al* (1979) have proposed a method to extract pseudopotentials from *ab initio* atomic calculations. The atomic potential is multiplied by a smooth short-range cut-off function which removes the strongly attractive and singular part of the potential. The parametrised cut-off function is adjusted numerically to yield eigenvalues equal to the atomic valence levels and nodeless eigenfunctions which converge identically to the atomic valence wavefunctions beyond a chosen core radius  $r_c$ . Furthermore, to reproduce the electrostatic and scattering properties of the real ion core with a minimum error, the 'pseudo' charge contained in the core region is forced to converge identically to the real charge in that region. The latter condition, which has not been discussed before, is shown to be essential to obtain a high-quality pseudopotential.

In this Letter we present an alternative approach which can be mostly carried out analytically. It is even simpler than the one proposed by Hamann *et al* (1979) and leads to pseudopotentials of at least the same quality. Because the construction of the pseudopotential is achieved by imposing certain conditions on the pseudo-wavefunction, it is reasonable to satisfy these conditions not via the potential but by directly modifying the atomic valence wavefunction. We therefore replace the actual shape of the atomic valence wavefunction inside the core region by a convenient analytical form

$$F(r) = rR(r) = r^{l+1}f(r) \quad (1)$$

where  $R(r)$  is the radial pseudo-wavefunction and  $l$  denotes the angular momentum quantum number. The function  $f(r)$  is chosen to give a smooth non-singular potential.

It may be a polynomial  $p(r)$ :

$$f(r) = \alpha r^4 + \beta r^3 + \gamma r^2 + \delta = p(r) \quad (2)$$

or an exponential

$$f(r) = \exp(p(r)). \quad (3)$$

The term linear in  $r$  is absent in  $p(r)$  to avoid a singularity in the pseudopotential at  $r = 0$ . To determine the coefficients in  $p(r)$  we apply the following conditions.

- (i) The real and 'pseudo' atom have the same valence eigenvalues for some chosen electronic configuration (usually the atomic ground state).
- (ii) The pseudo-wavefunction  $R(r)$  is nodeless and is *identical* to the real valence wavefunction at and beyond a chosen core radius  $r_c$ .
- (iii) Both the first and the second derivatives of the wavefunction  $F$  are matched to the real values at  $r_c$ .
- (iv) The pseudo-charge contained in the sphere with the radius  $r_c$  is identical to the real charge in that sphere.

Condition (i) and, in some less rigorous formulation, condition (ii) have been used in earlier attempts to obtain a reliable pseudopotential (Kerker *et al* 1978, Zunger and Cohen 1978). Condition (iii) ensures that the pseudo-wavefunction matches the atomic wavefunction continuously and differentially at  $r_c$ . The screened pseudopotential  $V_{ps}^s(r)$ , which is obtained analytically for  $r \leq r_c$  from the Schrödinger equation†

$$[-d^2/dr^2 + l(l+1)/r^2 + V_{ps}^s(r) - E] F(r) = 0 \quad (4)$$

is automatically matched continuously to the self-consistent atomic potential at  $r_c$ . Condition (iv), which was first introduced by Hamann *et al* (1979), guarantees that the pseudo-wavefunction is properly normalised. The total charge in the sphere with radius  $r_c$  is related to the first energy derivative of the logarithmic derivative of  $R$  at the sphere boundary (see Callaway 1964) by

$$-F^2 \frac{d}{dE} \frac{d}{dr} \ln R \Big|_{r=r_c} = \int_0^{r_c} F^2 dr. \quad (5)$$

Because of condition (iv) the first energy derivative of the pseudo-logarithmic derivative is identical to the exact result. As a consequence the scattering properties of the real ion core are transferred to the pseudo-core with minimum error.

Having set up the conditions which the pseudo-wavefunction must satisfy it is now straightforward to determine the analytical form  $f(r)$  as given in equations (2) or (3). Although a polynomial is easier to handle there is no guarantee that it would yield a nodeless wavefunction. We have therefore used equation (3) in the following examples. Conditions (i) to (iii) then read

$$\ln(P/r_c^{l+1}) = p(r_c) \quad (6)$$

$$r_c D = l + 1 + r_c p'(r_c) \quad (7)$$

$$r_c^2 V_c + (l+1)^2 - r_c^2 (E + D^2) = r_c^2 p''(r_c). \quad (8)$$

The prime denotes differentiation with respect to  $r$ . If we denote the amplitude of the atomic radial wavefunction times  $r$  by  $P(r)$ , we have  $P_c \equiv P(r_c)$  and  $D \equiv P'(r_c)/P(r_c)$ . The

† Atomic units are used throughout the paper.

value of the *atomic* potential at  $r_c$  is given by  $V_c$ ;  $E$  is the *atomic* valence eigenvalue for angular momentum quantum number  $l$ . Equations (6) to (8) are three linear equations for  $\alpha$ ,  $\beta$  and  $\gamma$  in terms of  $\delta$  which are easily solved analytically. From condition (iv) we obtain the equation

$$2\delta + \ln I - \ln A = 0 \quad (9)$$

where

$$I = \int_0^{r_c} r^{2(l+1)} \exp(2\alpha r^4 + 2\beta r^3 + 2\gamma r^2) dr \quad (10)$$

and  $A$  is the amount of *real* charge contained in the core region up to  $r = r_c$ . Equation (9) which determines the parameter  $\delta$  is the *only* equation to be solved numerically because there is no closed expression for the integral. It usually has one solution which can be found after a few iterations using, for example, the *regula falsi* method. From the

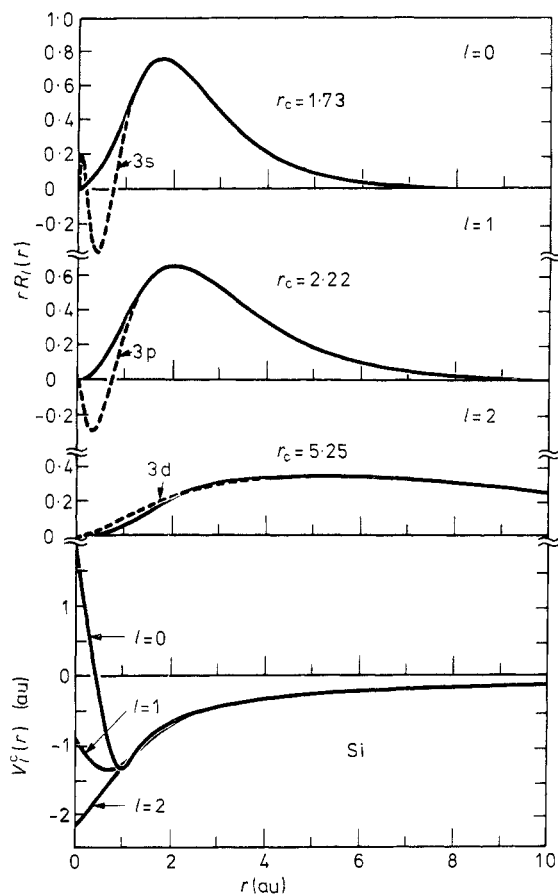


Figure 1. Real (broken curves) and pseudo- (full curves) radial wavefunctions for Si in the configuration  $3s^2 3p^1 3d^1$ . The angular components of the corresponding core pseudo-potential are also plotted. Note that the repulsive centrifugal potential is not included.

Schrödinger equation we find the screened pseudopotential in terms of the coefficients  $\alpha, \beta, \gamma$  by simple differentiation:

$$V_{\text{ps}}^s(r) = E + \lambda(2l + 2 + \lambda r^2) + 12\alpha r^2 + 6\beta r + 2\gamma \quad (11)$$

where  $\lambda = 4\alpha r^2 + 3\beta r + 2\gamma$ . As we have seen,  $V_{\text{ps}}^s(r)$  is completely determined by the atomic valence eigenlevel, by the value of the atomic potential at  $r_c$ , by the value of the amplitude and the logarithmic derivative of the atomic wavefunction at  $r_c$ , and by the real charge in the sphere with radius  $r_c$ .

So far nothing has been said about the choice of the core radius  $r_c$ . Since we are interested in transferring as much essential information as possible from the real atom to the pseudo-atom without sacrificing the conditions (i)–(iv), it is quite natural to choose  $r_c$  between the position of the outermost node and the position of the outermost extremum of the atomic radial wavefunction. It is also clear that condition (iv) cannot be satisfied if an exponential form is kept for  $f(r)$  in equation (1) and  $r_c$  is chosen too close to the outermost node position. It is therefore reasonable to use a value for  $r_c$  near the position of the outermost maximum of the radial charge. It turns out that the screened pseudopotential  $V_{\text{ps}}^s$  becomes 'softer' the closer  $r_c$  is taken at this position. Through the

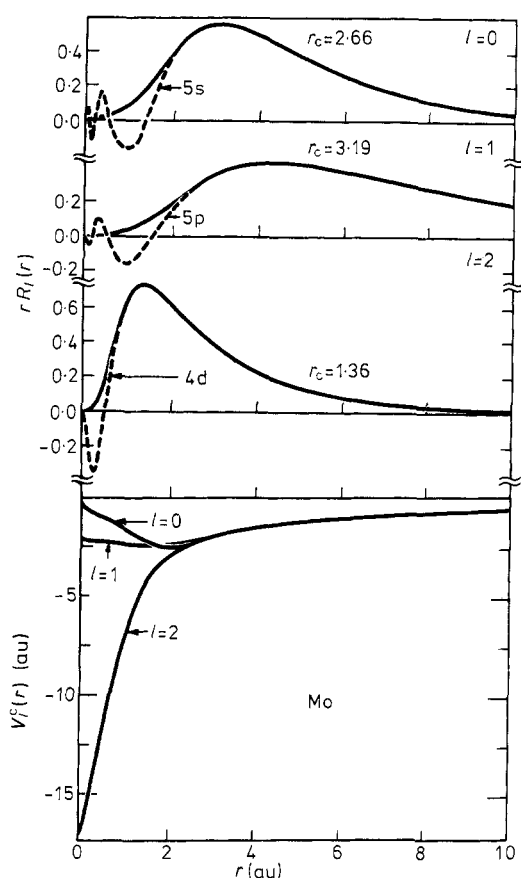


Figure 2. Real and pseudo-radial wavefunctions for Mo  $5s^1 4d^5 5p^0$  and the core pseudo-potential. Conventions are as in figure 1.

matching procedure required in condition (iii) and the choice of  $r_c$  the potential  $V_{ps}^s$  becomes dependent on the angular momentum quantum number.

From the pseudo-charge density we calculate a screening potential which is given as the sum of a Coulomb and an exchange and correlation part. The bare ion core pseudopotential is obtained by subtracting the screening potential from  $V_{ps}^s$ . We must of course assume the same electronic configuration for the pseudo-atom as for the real atom.

The efficiency of our method is illustrated in figures 1 and 2. Figure 1 shows the core pseudopotential for Si together with the radial valence wavefunctions for both the real and the pseudo-atom. We used the exchange-correlation potential of Hedin and Lundqvist (1971). In the Si atomic ground state the 3d orbital is not occupied. To obtain a d-like pseudopotential we have used the excited configuration  $3s^2 3p^1 3d^1$ , in which the 3d state is bound. The 3d wavefunction is already nodeless because there are no d states in the core. An electron in this state 'feels' the full atomic potential which has a singularity at  $r = 0$ . However, one can obtain a 3d soft-core pseudopotential by slightly changing the shape of the 3d wavefunction as indicated in the plot. Figure 2 is a similar plot and displays the wavefunctions and core pseudopotential for Mo in the configuration  $4d^5 5s^1 5p^0$ . While the s and p components of the core potentials are fairly weak, the d

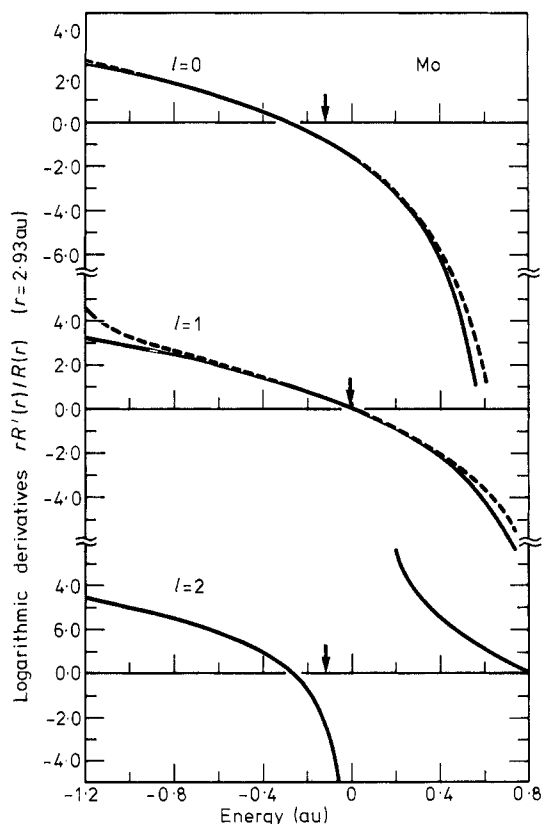


Figure 3. Energy dependence of the radial logarithmic derivative of the valence wavefunctions for Mo  $5s^1 4d^5 5p^0$  at  $r = 2.93$  au. The full curve refers to the pseudo-atom, the broken curve is the *ab initio* result. The arrows indicate the positions of the atomic levels.

component is strongly attractive and has its minimum at  $r = 0$ , in contrast to the potential given by Hamann *et al* (1979) and earlier published Mo pseudopotentials (Kerker *et al* 1978, Zunger and Cohen 1978). Although in all cases the chosen core radius  $r_c$  is practically equal to the position of the outermost maximum of the radial charge, condition (iii) guarantees that the pseudo-wavefunction is still very close to the real wavefunctions at positions at least 0.5 au inside  $r_c$  before it starts deviating from the exact result. This is also the reason why the pseudopotential does not show a noticeable kink at  $r_c$  even though we do not match the first derivative of the potential at  $r_c$ .

To demonstrate the transferability of the core pseudopotentials we compare in figure 3, in close analogy to Hamann *et al* (1979), the logarithmic derivative of the pseudo- and exact wavefunction for Mo at a radius close to the Wigner-Seitz radius. No noticeable deviation is found for  $l = 2$  in the energy range shown. For  $l = 0$  and  $l = 1$  we find a negligible deviation in an energy interval around the atomic level, which is of interest in most applications.

Comparison of the pseudo-eigenvalues of Ca, Si and Mo calculated for various excited atomic configurations different from the reference configuration with those of *ab initio* calculations shows that the differences are less than 0.005 au for all levels. Even the levels of singly and doubly ionised configurations are reproduced within this accuracy. Preliminary band structure calculations on bulk Ca, Si and Mo are in very good agreement with results obtained by different methods and confirm the transferability of our pseudopotentials.

We conclude that by using a suitably chosen parametrisation of the core part of the pseudo-valence wavefunction one can set up a procedure to construct pseudopotentials which is so simple that it can mostly be carried out analytically. The resulting pseudopotentials are of at least the same quality as the potentials obtained by a recent approach suggested by Hamann *et al* (1979). They are 'soft' enough to be useful in band structure calculations employing momentum space techniques which rely on a fast convergence.

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