

# FULL DEVELOPMENT OF PSEUDOPOTENTIALS THAT WORK FOR ALL ELEMENTS

Laz Ezenwaka

Department of Industrial Physics, Anambra State University, Uli, Nigeria.  
E-mail : ngocee@yahoo.com

(Submission: 30 January, 2007; Accepted: 3 June, 2007)

## Abstract

*The form factors of pseudopotential that works for all elements is fully developed. The plane wave matrix element of pseudopotential is evaluated. In addition, the linear coefficients parameter  $A_i$  are calculated by the use of tables of Bachelet et al. (1982) as well as the prescription of Pattnaik et al. (1979) which eliminated the numerical instability problems. The liquid metal resistivity is evaluated using Simpson's rule.*

**Key words:** *Pseudopotential, liquid metal resistivity, matrix element, linear coefficients, inverse orthogonality transformation.*

## 1. Introduction

For many years it was known that quite good, quantitative treatments of some properties of metals have been obtained by applying the free electron theory. This theory presumes the electrons to roam through the metal at will. The core region of every metal contains strong force fields which must greatly perturb as conduction electron penetrating it, in apparent contradiction of the free electron theory. Nevertheless, the old nearly free electron model of Mott and Jones (1985) had a strong measure of success in predicting metallic properties without a great deal of theoretical justification. In the free electron approximation the forces between the conduction electrons and ion cores are neglected; all calculations proceed as if the conduction electrons were free to move everywhere within the specimen. The total energy is all kinetic, the potential energy is neglected. In any case, the theory is useful for experiments that depend mainly on the kinetic properties of the conduction electron. The pseudopotential theory to some extent vindicates the nearly free electron theory, puts it on a firmer physical footing, and gives a new mathematical procedure for the calculation of many properties of metals. It must be stressed that pseudopotential theory as been successfully applied to 'normal'

metals at the beginning, that is, those metals whose ion cores do not overlap in the crystalline state. In the empirical pseudopotential method, the band structure of semi conductors and simple metals were given. In this method, the local effective potential acting on the electrons, including coulomb and exchange – correlation contributions as well as the ionic parts, was represented by just a few terms in a fourier expansion. The coefficients were adjusted to agree with some experimentally determined features of the energy bands. But a later approach was given by Bachelet et al (1982) in which a simple function representing the ion-core potential was adjusted to fit the experimental ionization potential of the hydrogenic ion. In any case, the wave functions of Philips and Kleinmann (1959) pseudopotentials have their own problem of orthogonality hole which puts too much of its total charge in the core region.

In this paper, the Fourier transform of pseudopotentials that work is fully developed. In addition, the linear coefficients parameters  $A_i$  are calculated using plane wave matrix element of the pseudopotential. The liquid metal resistivities of transition metals were calculated using Simpson's rule. In the calculation, we employed Bachelet approach (1982).

## 2. Fourier Space Evaluation of the Pseudopotential

The matrix element between plane waves of the pseudopotential given by

$$\langle k | V_1^{\text{ion}}(r) | k+q \rangle = 1/\Omega \int_0^\infty \int_0^{2\pi} \int_0^\pi e^{-ik \cdot r} V_1^{\text{ion}}(r) e^{+i(k+q) \cdot r} r^2 dr \sin\theta \, d\theta \, d\phi \tag{1}$$

where  $k$  is the wave vector of the scattered electron  $V_{\text{ion}}$  of ionic potential,  $q$  is the

scattering vector,  $\Omega$  is the atomic volume and  $V_{\text{core}}$  is the core potential

$$\langle k | V_1^{\text{ion}}(r) | k+q \rangle = 1/\Omega \int_0^\infty \int_0^{2\pi} \int_0^\pi V_1^{\text{ion}}(r) e^{iq \cdot r} r^2 dr \sin\theta \, d\theta \, d\phi \tag{2}$$

$$= 1/\Omega \int_0^\infty \int_0^{2\pi} \int_0^\pi [V_{\text{core}}(r) + \Delta V_1^{\text{ion}}(r)] e^{iq \cdot r} r^2 dr \sin\theta \tag{3}$$

where  $V_{\text{core}}(r) = Zv/r \{ \sum C_i^{\text{core}} \text{erf}[(\alpha_i^{\text{core}})^{1/2} r] \}$

and  $\Delta V_1^{\text{ion}} = \sum_{i=1}^3 (A_i + r^2 A_i + 3) e^{-\alpha_i r^2}$

with  $Zv$  as the valence charge of each atom,  $C_i^{\text{core}}$ ,  $\alpha_i^{\text{core}}$ ,  $i = 1, 2$  are the linear core coefficients and decay constant respectively, and  $A_i$  of  $A_i + 3$  with  $\alpha_i = 1, 2, 3$  are also linear coefficients and decay constants.

A similar expression is written for spin-orbit part of the potential  $V_i^{\text{so}}(r)$ , where applicable. The above integral in eqn. (3) can be reduced to

$$V_1^{\text{ion}}(q) = 1/\Omega 4\pi/q \int_0^\infty V_1^{\text{ion}}(r) r dr \sin qr \tag{4}$$

Substituting eqn. (3) into eqn. (4), we get:

$$V_1^{\text{ion}}(q) = -4\pi/\Omega q \int_0^\infty Zv \{ \sum C_i^{\text{core}} \text{erf}[(\alpha_i^{\text{core}})^{1/2} r] \} r \sin qr \, dr + 4\pi/\Omega q \sum A_i \int_0^\infty e^{-\alpha_i r^2} r \sin qr \, dr + 4\pi/\Omega q \sum A_{i+3} \int_0^\infty e^{-\alpha_i r^2} r^3 \sin qr \, dr \tag{5}$$

Thus, we have three (3) integrals to evaluate as follows:

$$\begin{aligned} I_1 &= \int \text{erf}[(\alpha_i^{\text{core}})^{1/2} r] \sin qr \, dr = 1/q e^{-q^2/4\alpha_i^{\text{core}}} \} \\ I_2 &= \int e^{-\alpha_i r^2} r \sin qr \, dr = q\sqrt{\pi}/4\alpha_i^{1/2} \exp(-q^2/4\alpha_i) \} \\ I_3 &= \int e^{-\alpha_i r^2} r^3 \sin qr \, dr = \sqrt{\pi} (6q\alpha_i - q^3)/16\alpha_i^{7/2} \exp(-q^2/4\alpha_i) \} \end{aligned} \tag{6}$$

Therefore, for each angular momentum, we have

$$V_1^{\text{ion}}(q) = -4\pi Zv/\Omega q^2 \sum C_i^{\text{core}} e^{-q^2/4\alpha_i^{\text{core}}} + \pi^{3/2}/\Omega \sum A_i/\alpha_i^{3/2} e^{-q^2/4\alpha_i} + 4\pi^{3/2}/\Omega 4 \sum_{i=1}^2 A_{i+3}/\alpha_i^{7/2} (6\alpha_i - q^2) e^{-q^2/4\alpha_i} \tag{7}$$

Thus, the total ionic pseudopotential is given by a sum over the angular momenta:

$$\begin{aligned}
 V_{ps}^{ion}(q) = \sum V_i^{ion}(q) = & -4\pi Zv/\Omega q^2 \sum C_i^{core} e^{-q^2/4\alpha_i^{core}} \\
 & + \sum_{l=1}^2 \{ \pi^{3/2} / \Omega [A_{il}/\alpha_{il}^{3/2} e^{-q^2/4\alpha_{il}} + A_{2l}/\alpha_{2l}^{3/2} e^{-q^2/4\alpha_{2l}} \\
 & + A_{3l}/\alpha_{3l}^{3/2} e^{-q^2/4\alpha_{3l}} + \pi^{3/2}/4\Omega [A_{4l}/\alpha_{4l}^{7/2} (6\alpha_{4l}-q^2) e^{-q^2/4\alpha_{4l}} \\
 & + A_{5l}/\alpha_{5l}^{7/2} (6\alpha_{5l}-q^2) e^{-q^2/4\alpha_{5l}} + A_{6l}/\alpha_{6l}^{7/2} (6\alpha_{6l}-q^2) e^{-q^2/4\alpha_{6l}}] \} \quad (8)
 \end{aligned}$$

We have obtained the ionic pseudopotential in momentum space and there is need to obtain the parameter  $A_j$  which is the linear coefficients.

**3. Determination of the Parameter  $A_j$**   
 Linear dependencies of the fitting functions can lead to large values for some of the fitting coefficients  $A_j$  in the potential.

$$\Delta V_l^{ion}(r) = \sum_{i=1}^2 (A_i + r^2 A_i + 3) e^{-\alpha_i r^2} \quad (9)$$

Thus each atom is characterized by:

- (i) a valence charge  $Zv$  and two sets of linear coefficients and decay constant describing the core,  $C_i^{core}$ ,  $\alpha_i^{core}$ ,  $i = 1, 2$

where,

$$C_1^{core} + C_2^{core} = 1$$

- (ii) For each  $l$  value two sets of three linear coefficient each,  $A_j$  and  $A_j + 3$

$$A_i = \sum_{j=1}^2 C_j Q_{ij}^{-1} \quad (10)$$

corresponding to the decay constants  $\alpha_j = 1, 2, 3$  for the average potential, provided the spin orbit splitting of the eigen values is larger than a chosen threshold value of 0.05eV.

In order to obtain the linear coefficients  $A_j$  to be used in calculation, the coefficients  $C_j$  have to be transformed by an inverse orthogonality transformation

The  $C_j$  parameters as tabulated by Bachelet *et al* (1982). (Table 1) are used in the calculation of  $A_j$ . Nonetheless, too many significant figures must be retained in the  $A_j$ 's for practical

tabulations. To solve this problem, we have transformed the coefficients  $A_j, A_j + 3, j = 1, 3$  of eqn. (10) into a set of coefficients  $C_j, j = 1, 6$  for an orthonormal bases set;

$$C_i = \sum A_j Q_{ij} \quad (11)$$

Table 1: The Ci parameters as tabulated by Bachelet et al. (1982)

Atom	Zv	l	$\alpha_1$	$\alpha_2$	$\alpha_3$	C1	C2	C3	C4	C5	C6
Cu	1	Core	7.9500	3.0200		2.6959	-1.6959				
		0	1.7500	2.3200	3.0900	-7.2915	-1.4275	-0.8717	0.3180	-0.5590	0.0289
		1	1.2500	7.8000	10.9300	-5.8592	-2.6799	0.6113	0.1380	-0.2028	-0.0691
		2	2.7800	25.7000	27.4700	1.7433	3.0667	0.7516	0.2538	-0.2938	0.1973
		So <sub>1</sub>	0.5400	1.4400	1.7300	-0.0347	0.0022	0.0035	0.0029	-0.0008	-0.0003
		So <sub>2</sub>	19.5500	28.1600	37.6100	-0.0158	-0.0042	0.0012	0.0004	0.0000	0.0001
Pb	4	Core	1.9200	0.7600		8.5444	-5.8444				
		0	1.4000	1.9800	3.5700	-8.3628	0.01094	0.1191	0.3305	0.0557	0.0032
		1	0.9500	1.2100	1.7700	-6.9590	-0.5127	0.0637	0.2131	0.0485	-0.0143
		2	0.7900	0.9100	1.2000	-6.8182	-0.8903	-0.6033	0.1888	0.02154	0.0916
		3	1.3500	1.6200	1.8200	-4.0362	-1.0178	0.5641	0.1487	-0.1291	-0.0624
		So <sub>1</sub>	0.4500	0.7100	0.8200	-0.5058	-0.0654	0.04877	-0.0128	0.0136	-0.0117
So <sub>2</sub>	0.240	0.3000	0.4000	0.0257	0.0759	0.0376	0.0130	-0.0275	0.0245		
Bi	5	Core	2.0300	0.8100		5.2104	-4.2104				
		0	0.6200	2.1600	3.2400	-8.6521	0.5682	0.0727	0.2679	0.0221	-0.0041
		1	1.230	1.4800	1.7500	-7.2503	0.3928	-0.0127	0.1712	0.0669	-0.0059
		2	0.9200	1.0400	1.3400	-7.0492	-0.4597	-0.5518	-0.2095	0.0055	0.0813
		3	1.7000	1.9200	2.1900	-3.6420	-0.7705	0.05327	0.0841	-0.1722	-0.0752
		So <sub>1</sub>	0.4700	0.7700	0.8900	-0.5574	-0.0931	0.0509	-0.1140	0.0107	-0.0147
So <sub>2</sub>	0.2800	0.3400	0.4500	0.0246	0.0777	0.0401	0.0112	-0.0260	0.0260		
TL	3	Core	1.7700	0.5900		6.7158	-6.7158				
		0	1.2400	1.8900	5.0700	-7.6582	-0.0300	0.1161	0.3351	0.0637	-0.0059
		1	0.7100	0.9600	1.3000	-5.8681	-1.0109	-0.0109	0.0245	0.0178	-0.0129
		2	0.7000	0.8100	1.0400	-6.0798	-0.8199	-0.5486	-0.1761	0.0331	0.1048
		3	0.9100	1.0900	1.2100	-4.1125	-1.3267	0.4578	0.1868	0.0910	-0.0456
		So <sub>1</sub>	0.3100	0.5200	0.6200	-0.3984	-0.1040	0.0451	-0.0222	0.0174	-0.0109
So <sub>2</sub>	0.2000	0.2400	0.3200	0.0288	0.0753	0.0435	0.0094	0.0219	0.0369		
Ni	2	Core	7.6000	2.7400		2.6949	-1.6949				

	0	1.800	2.3800	3.1700	-7.5612	-1.1572	0.8213	0.2546	-0.351	0.0220
	1	1.1800	2.1000	2.5900	-5.8322	-2.4306	-1.2453	0.2729	-0.1929	0.1633
	2	2.5800	23.5500	26.6000	1.5867	2.9229	-0.6560	0.2811	-0.2986	0.1867
	SO <sub>1</sub>	0.5100	1.2900	1.500	-0.0324	0.0022	0.0034	0.0025	-0.0008	-0.0003
	SO <sub>2</sub>	18.010	24.1700	31.7500	-0.0155	-0.0044	0.0016	-0.008	0.0001	0.0002

Table 2: Ai results for copper, lead, bismuth, thallium and nickel atoms  
[Cu]

L	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>
O	66.03779	-123.17795	99.83706	-2.82897	0.35245	0.034565
1	10.29377	70.43324	-41.06683	0.13694	25.34715	9.25869
2	3.27978	-806.42524	732.52223	-5.32135	121.38282	-124.84925
SO <sub>1</sub>	-123.17795	99.83706	-2.82897	0.35254	-0.34565	1.75000
SO <sub>2</sub>	70.43324	-41.06683	0.13694	25.34715	9.25869	1.25000

## [Pb]

L	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>
O	34.15055	-5.67858	-2.61607	-2.60972	-0.49116	-0.04965
1	14.15523	5.48528	-1.20937	-1.23535	-0.17929	0.06744
2	51.65715	-75.47792	43.03156	0.37112	-0.35745	-0.20105
3	-5.67858	-2.61607	-2.60972	-0.49116	-0.04965	1.40000
SO <sub>1</sub>	5.48528	-1.20937	-1.23535	-0.17929	0.06744	0.95000
SO <sub>2</sub>	-75.47792	43.03156	0.37112	-0.35795	-0.20105	0.79000

## [Tl]

L	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>
O	27.79250	-4.57524	-1.28774	-2.322459	-0.47952	-0.04965
1	11.06046	-0.34763	3.67954	-1.39628	-0.05991	0.06744
2	44.66191	-66.21326	37.29997	0.19264	-0.49985	-0.20105
3	-4.51524	-1.28774	-2.32459	-0.47952	0.21272	1.40000
SO <sub>1</sub>	-0.34763	3.67954	-1.39628	-0.05991	0.02553	0.95000
SO <sub>2</sub>	-66.21326	-37.29997	0.019264	-0.49985	-0.76854	0.79000

## [Bi]

L	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>
O	47.21382	-16.76466	-2.56942	-2.32355	-0.17881	0.05299
1	43.20601	-29.38373	6.05858	-1.29180	-0.34902	0.02958
2	78.07395	-109.36503	51.71981	0.57288	-0.28227	-0.27460
3	-16.74680	-2.56942	-2.32355	-0.17881	0.02599	1.62000
SO <sub>1</sub>	-29.38378	6.05858	-1.29180	-0.34902	0.02958	1.23000
SO <sub>2</sub>	-109.36503	51.71981	0.57288	0.28227	-0.27246	0.92000

[Ni]

L	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>
O	70.16069	-123.18541	95.68410	-2.42012	-1.75485	-0.28523
1	25.36635	-116.45741	128.44245	-1.75485	0.70833	-1.55453
2	3.63909	-421.45741	354.46514	-5.04577	114.10574	-112.52278
3	-123.18541	95.68410	-2.42012	-1.75485	-0.28523	1.80000
SO <sub>1</sub>	-116.45741	128.44245	-1.75485	0.70833	-1.55453	1.18000
SO <sub>2</sub>	-421.45741	354.46514	-5.04577	114.10574	-112.52278	1.08234

**Application in Solid State Physics (liquid metal resistivity)**

The electrical resistivity of liquid transition metals is given by the Ziman's formula (Ziman,1961)

$$\rho = \frac{3\pi\Omega_0}{e^2 h V_f K_f^4} \int S(q) |V(q)|^2 q^3 dq \tag{12}$$

where  $\Omega_0$  is the atomic volume,  $V_f$  is the velocity of the electron at Fermi level,  $S(q)$  is the Structure Factor, and  $V(q)$  is the form factor of the single ion potential. The calculation of liquid metal resistivity can be done once the function  $[V(q)]^2$  is determined eqn. (8), The model potential parameters developed by Animalu and Heine (1965) were used in the calculations.

**Table 3:** Model potential parameters used for the calculation of liquid metal resistivity for copper, lead, bismuth, thallium and nickel.

Element	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	R <sub>M</sub>	Ω	Z	M*	K <sub>f</sub>	(½W) <sup>2</sup>	dA <sub>0</sub> /dE	2dA <sub>0</sub> /dE	dA <sub>2</sub> /dE	α
Cu	0.6064	0.6070	0.6640	2.2000	78.900	1.000	1.000	0.720	0.017	0.201	0.610	0.774	0.654
Pb	1.9040	1.6320	1.7250	2.1010	203.40	4.000	1.000	0.835	0.058	0.517	0.756	0.378	0.205
Bi	2.3900	2.6130	0.2590	2.0920	239.40	5.000	1.000	0.852	0.058	0.547	1.156	0.846	0.174
Tl	1.5110	1.6320	1.0880	1.9860	191.70	3.000	1.000	0.774	0.058	0.450	0.256	0.096	0.348
Ni	0.6104	0.6107	0.6460	2.2000	73.600	1.000	1.000	0.925	0.023	0.605	1.000	1.844	0.584

**Table 4:** Experimental and calculated values for liquid metal resistivity for copper, lead, bismuth, thallium and nickel (in units of ohm – cm).

Liquid metals	Experiment value Faber (1977)	Calculated value
Cu	21.00	22.45
Pb	95.00	93.86
Bi	128.00	127.70
Tl	73.00	74.15
Ni	85.00	87.20

The liquid metal resistivity of copper, lead, bismuth, thallium and nickel were computed. The results obtained are shown in Table 4, where they are compared with experimentally

obtained values. It is observed that the calculated results are in good agreement with experimentally obtained results.

## 5. Results and Discussion

A good achievement that was made is the evaluation of plane wave matrix element of pseudopotential that works for the elements. In addition, we calculated the linear coefficient parameters  $A_i$  by the use of Table 1 of values of Bachelet et al. (1982) as well as the prescription of Pattnaik et al (1979) which eliminated the numerical instability problems. The results of  $A_i$  are shown in Table 2. Values of  $A_i$  for the transition elements were calculated. During the calculation of the values of  $A_i$  for each element, we encountered a problem of not obtaining any result for quantum number  $l = 2$ . The problem has to do with obtaining a negative at the square root function which the computer system used regards as illegal square root function. This bottle-neck was overcome by putting a modular in all the square root function. The  $A_i$ 's calculated were used to carry out some checks with Nickel and  $V_s(q)$  behave as is expected in the limit as  $q \rightarrow 0$ .

Even though, with the advent of pseudopotential theory, it is possible to devise, say, a form of real-space two-body interatomic potential, but this is only a small part of the theory. For there are many problems which could be tackled using, for example, this pair potential which could be solved in principle in a fourer space approach and this is what we have tackled in this work. Also the phonon frequency and liquid metal resistivity computations can now be achieved with the subject matter of this work.

For the present calculation, we have used the model potential derived from spectroscopic term values by Animalu and Haine (1965). These values of model potential are tabulated in Table 3. We can thus see that this modified form of the model potential has the advantage that it includes both a repulsive exchange overlap (core-core) part, an attractive part that takes into account  $s-d$  hybridization, and is purely columbic outside the parametric radius  $R_m$ . For screening we used the simple Thomas-fermi type of dielectric function which is quite adequate for liquid metal resistivity calculations to ensure that  $-2/3E_f$  limit as  $q$  tends to zero. We have developed a comprehensive and consistent pseudopotentials that work form factors for the computation of various condensed matter properties. Our goal has been to discuss the physics of the pseudopotentials that work

form factor and then apply the form factor in the calculation of various solid state properties. We have applied the form factor in calculation of the liquid metal resistivity for five metals and the results obtained are tabulated in Table 4 where they are compared with the experimentally obtained results Faber (1977). The calculated results are in good agreement with the experimental results.

The pseudopotentials that work calculations are rigorous, extensive and detailed, but that price is worth paying for considering the accuracy with which theoretically calculated results agreed with the experimental results. It is therefore an elegant method and it is anticipated that this form factor developed will continue to be useful in many contexts.

The result of this work provide exciting insight to many applications as proposed by Slater (1937). Today, we have found a key-computational physics on the computer – that is providing the answers to many questions raised by pseudopotentials that work critiques. We are convinced that as computational physics and computers continue to evolve, the expansion of research on even more complex systems will become possible using the pseudopotentials that work method. The rigorous, extensive and lengthy calculations involved in the pseudopotentials that work method is now an advantage because the method is detailed, and there was no local field corrections and the results of the liquid metal resistivities calculated were in good agreement with the experimental results. It is our belief that the application of the pseudopotentials that work form factors to other phenomena like phonon frequencies, optical properties etc. will not be different.

## References

- Animalu, A. O. E. and Heine, V. (1965): Optimized Model Potential Parameters in Metals, *Phy. Mag.* A12, 129.
- Bachelet, G. B., Harmann, D. R. and Schluter, J. C. (1982): Pseudopotentials that Work from H to Pu, *Phy. Rev.* B24 – 4745.
- Faber, T. E. (1977): Introduction to the Theory of Liquid Metals, Cambridge University Press.

- Faber, T. E. and Ziman, J. M. (1968): Plane Waves Pseudopotentials and the L.A.P.W. Method. *Phil. Mag.* 11, 153.
- Mott, N. F. and Jones, E. A. (1985): *Theory of the Properties of Metals and Alloys*, Oxford University Press (Clarendon).
- Philips, J. C. and Kleinmann, L. (1959): Temperature Dependence of Residual Electrical Resistivity of Cu-Au in Pseudopotentials Approximation, *Journal of Phy. Rev.* 116, 287.
- Slater, J. C. (1937): Application of Pseudopotential Theory to Noble and Transition Metals, *Phy. Rev.* 51, 546.
- Pattnaik, P. C., Fleteher, G. and Fry, J. L. (1979): Finite Mean-Free Paths and the Electrical Resistivity of Liquid Simple Metals and Binary Alloys, *Phy. Rev.* B28.
- Ziman, J. M. (1961): Surface Green Function Matching (SGFM) Applied to the Calculation of Surface band Structure of V., *Phil. Mag.* 6, 1013.