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Calculation of liquid metal resistivity for lithium, sodium, potassium, calcium and zinc using pseudopotential form factors

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Abstract

The pseudopotential form factors developed by Ezenwaka (2007) were used to calculate the liquid metal resistivity for Lithium Sodium, Potassium, Calcium, and Zinc. In addition, the linear coefficients parameter Ai were calculated by the use of data of Bachelet et al (1982) as well as the prescription of Pattnaik et al (1979) which eliminated the numerical instability problems. The liquid resistivity is evaluated using Simpson's rule. The results obtained theoretically were compared with experimentally observed results of Faber (1977) and 88% good agreements were obtained within the framework of the calculations.
Keywords: Pseudopotential, Form factors, Resistivity, Matrix element, Linear coefficients,

1. Introduction

Pseudopotentials were originally introduced to simplify electronic structure calculations by eliminating the need to include atomic core states and the strong potentials responsible for building them. Considerable success was achieved in describing the band structure of semi conductors and simple metals with the use of the empirical pseudopotential method (Philips and kleiman, 1959)

Mott and Jones (1985) adjusted the potential coefficients to agree with some experimentally determined features of the energy band. In this approach, the total effective potential acting on the electrons including coulomb and exchange correlation contributions as well as ionic parts were represented by just a few terms in a Fourier expansion. Slater (1937) formulated the band structure methods based on Muffin-tin potential such as the augmented – plane wave (APW) methods and karringa-kolin –Rostoker (KKR) method which depend only on the logarithmic derivatives of the potential at the muffin-tin-radius. But these methods are not customarily used for pseudopotentials.

But a later approach was given by Bachelet et al (1982) in which a set of non conserving ion-core pseudopotentials for all elements in the periodic table were given. The transferability of these pseudopotentials makes them quite useful in calculations involving the electronic properties of molecules, solids and surfaces. The usefulness of the parameters given is further enhanced by the choice of the basis functions for parametric representation of the potential. The use of error functions and Gaussians as basic functions for the potential leads to analytical expressions for the matrix elements for both plane-wave and Guassian base sets for the wave functions. Thus the choice of the basic function for the parametric expression of the pseudoptential enables a speedy and narrative evaluation of the matrix elements. In order to obtain the linear coefficients Ai to be used in calculation, the coefficients, C_i have to be transformed by an inverse orthogonality transformation shown in equation (1).

$$A_i = \sum_{i=1}^{2} C_i Q_{il}^{-1} \quad - - \quad - \quad - \quad 1$$

Where i is the ion core patential

Pattnaik (1983) prescribed the use of explicit expressions for the inverse of orthogonality transfer matrix Q. The

analytical expressions for the elements of Q^{-1} enable us to directly calculate the parameters Ai from the calculated Ci parameters by the use of computer.

The interest to revisit the Backelet approach (1982) is motivated by the current numerical computation of electronic properties of condensed matter which has taken on an increased momentum with the new age of advanced computer logarithms using computers. Our intention is to use developed pseudopotential form factors (Ezenwaka, 2007) in the computation of various solid state properties like liquid metal resistivities which could not be calculated using the Philips and Klemann form (1959).

2 THE MATRIX ELEMENT OF THE PSEUDOPOTENTIAL FORM FACTORS

The matrix element between plane waves of the pseudopotential is given by

$$\angle K| v_1^{ion}(r) | k+q\rangle = 1/\Omega \int_0^{\infty}\int_0^{2\pi}\int_0^{\pi} e^{-ik.r} V_i^{ion}(r)\, e^{+i(k+q).r}\, d_c \quad - - (2)$$

Where k is the vector of the scattered electron V_{ion} of ionic potential, q is the scattered vector, Ω is the atomic volume and V_{core} is core potential

$$\angle K| v_i^{ion}(r) | K+q\rangle = 1/\Omega \int_0^{\infty}\int_0^{2\pi}\int_0^{\pi} V_I^{ion}(r)\, e^{iq.r}\, r^2\, dr \sin\theta\, d\theta\, d\Phi$$

$$= 1/\Omega \int_0^{\infty}\int_0^{2\pi}\int_0^{\pi} [V_{core}(r) + \Delta V_i^{ion}(r)]\, e^{iq.r}\, r^2\, dr \sin\theta \quad - (3)$$

Where $V_{core}(r) = Zv/r \{\Sigma C_i^{core} \operatorname{erf}[(\alpha_i^{core})^{1/2} r\}$

and $\Delta v_1^{core} = \sum_{i-1}^{3} (A_i + r^2 A_i + 3)\, e^{-air^2}$

With Zv as the valence charge of each atom, C_i^{core}, α_i^{core} i = 1, 2 are the linear core coefficient and decay constant respectively, and A_i of A_i +3 with α_i = 1,2,3 are also linear coefficients and decay constants. A similar expression is written for spin-orbit part of the potential $V_i^{so}(r)$ where applicable. The above integral in equation (3) can be reduced to

$$V_1^{ion}(q) = 1/\Omega\, 4/q \int_0^{\infty} v_i^{ion}(r)\, r dr \sin qr \qquad (4)$$

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

$$V_1^{ion}(q) = 4\pi/\Omega q \int_0^{\infty} Zv \{\Sigma c_i^{core} \operatorname{erf}[(\alpha_i^{core})^{1/2} r]\}\, r \sin qr dr$$

$$+ 4\pi/\Omega q\, \Sigma A_i \int e^{-air^2} r^3 \sin qr dr$$

$$+ 4\pi/\Omega q \Sigma A_i + 3 \int e^{-air^2} r^3 \sin qr dr \quad - - - \quad (5)$$

Thus, we have three integrals to evaluate as follows:

$I_1 = \int \operatorname{erf}[(\alpha_i^{core})^{1/2} r] \sin qr = 1/q\, e^{-q2}/4^{\alpha}{}_i^{core}$

$I_2 = \int e^{-\alpha ir^2} r \sin qr = q\, \pi^{1/2} \exp(-q^2)/4^{\alpha}{}_I$

$I_3 = \int e^{-\alpha ir^2} r^3 \sin qr\, dr = \sqrt{\pi}(6q\alpha - q^3)/16\alpha i^{7/2} \exp(-q^2/4^{\alpha}{}_I)$ (6)

Therefore, for each angular momentum, we have

$$V_i^{ion}(q) = -4\pi Zv/\Omega q^2 \Sigma C_i^{core} e^{-q2}/4\alpha_I^{core}$$

$$+\pi^{3/2}/\Omega \sum_{i=1}^{2} \{A_i/\alpha^{3/2} e^{-q^2/4\alpha_I^{core}}\}$$

$$+ 4\pi^{3/2}/\Omega\, 4\Sigma \sum_{i=1}^{2} A_i/ +3/\alpha_i^{7/2} (6\alpha_i - q^3) e^{-q2}/4\alpha_I \quad - \qquad (7)$$

3. PSEUDOPOTENTENTIAL FORM FACTORS

The total ionic pseudoptential was evaluated by Ezenwaka (2007) by a sum over the angular momenta from equation (7) and developed the pseudopotential form factors:

$$V_{ps}^{ion} = \sum v_i^{(ion)}(q) = \frac{-4\pi Zv}{\Omega q^2} \sum C_i^{core} e^{-q2}/4\alpha_I^{core}$$

$$+ \sum_{i=1}^{2} \left\{ \frac{\pi^{3/2}}{\Omega} \left(\frac{A_1 l\, e^{-q2}}{\alpha_i l^{3/2}} \Big/ 4\alpha_{il} + \frac{A_2 l}{\alpha_i l^{3/2}} \right) \left(e^{-q2}\ 4\alpha^2 l \Big/ \right) \right.$$

$$+ \frac{A_2 l}{\alpha_3 l^{3/2}} e^{-q2}/4\alpha_3 l + \frac{\pi^{3/2}}{4\Omega} \left(\frac{A_2 l}{\alpha_i l^{7/2}} (6\alpha_i l^{-} q^2)\, e^{-q2}/4\alpha_i l \right)$$

$$+ \frac{A_5 l}{\alpha_2 l^{7/2}} (6\alpha^2 l^{-} q^2) e\text{-}q^2/4\alpha_2$$

$$+ A_{6i}/\alpha_3 l\, (6\alpha_3 l^{-} q^2)\, e\text{-}q^2/4\alpha_2 l \quad - \quad - \qquad (8)$$

The pseudopotential form factors are obtained in momentum space and there is need to obtain the parameters Ai which are the linear coefficients.

4. DETERMINATION OF THE PARAMETER A_i

Linear dependencies of the fitting functions can lead to large values for some of the fitting coefficient Ai in the potential.

$$\Delta V_i^{core} = \sum_{i=1}^{2} A_i + r^2 A_i + 3)\, e^{-\alpha ir^2}$$

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}, α_i^{core}, I = 1, 2

where,
$C_i^{core} + C_2^{core} = 1$

ii. For each i value, two sets of three linear coefficients each A_i and $A_i + 3$ corresponding to the decay constants $\alpha_i = 1, 2, 3$ for the average potential, provided the spin orbit splitting of the eigenvalues is larger than a chosen threshold value of 0.05ev. In order to obtain the linear coefficients A_i to be used in calculation, the coefficients C_i have to be transformed by an inverse orthogonality transformation

$$A_i = \sum C_i Q_i l^{-1} \mathbf{2} \quad - - \quad - \quad (9)$$

i=1

The C_i parameters as tabulated by Bachelet et al (1982) in Table 1 are used in the calculation of A_i. Nevertheless, too many significant figures must be retained in the Ai' s for practical tabulations. To solve this problem, we have transformed the coefficients A_i, $A_i + 3$, i = 1, 3 of equation (9) into a set of coefficients C_i 1 = 1, 6 for an orthonomal bases sets;

$$C_i = \sum \Delta_i Q_{il} \quad - \quad - \quad - \quad (10)$$

Table 1: The C_i parameters as tabulated by Bachelet et al (1982) for Lithium, Sodium Potassium, Calcium and Zinc.

Atom	Z_v	*L*	α_1	α_2	α_3	C_1	C_2	C_3	C_4	C_5	C_6
L_i	1	Core	1.84	0.73		2.9081	-19081				
		0	1.10	1.23	1.42	-1.4520	0.2543	0.0381	0.0581	-0.004	-0.0114
		1	2.48	7.42	8.20	-0.0046	-0.1402	0.1055	0.1259	0.0241	0.0122
		2	0.33	0.46	0.62	06347	-0.5406	-01712	-0.0055	-0.0300	0.0316
Na	1	Core	1.71	0.50		5.1815	-4.1815				
		0	0.99	1.10	1.24	-2.4718	0.3334	0.0619	0.0890	-0.0041	-0.0123
		1	0.51	0.65	0.84	-1.6202	-0.4908	-0.0861	0.0375	-0.0161	0.0070
		2	0.38	0.55	0.73	-0.9415	-0.9710	-0.2336	-0.0593	-0.0228	0.0455
K	1	Core	1.42	0.26		6.3140	-5.3140				
		0	0.58	0.64	0.71	-3.9287	0.2938	-0.0613	0.1062	0.0000	-0.0092
		1	0.39	0.56	0.73	-3.2276	-0.4254	-0.1754	0.0803	0.0067	0.0111
		2	2.84	3.12	55.36	2.0774	-0.7044	-0.1248	-0.3174	-0.0802-	-0.0004
Ca	2	Core	1.61	0.45		4.8360	-3.8360				
		0	0.75	1.19	2.08	-4.7576	0.3179	-0.1286	0.0279	0.0520	0.0054
		1	0.67	2.23	2.99	-4.1513	0.0156	-0.1494	-0.2563	-0.0404	-0.0179
		2	6.92	24.35	86.59	3.0392	-1.0190	0.2634	0.4961	-0.0295	0.0089
Zn	2	core	8.38	3.49		2.6313	-1.6313				
		0	2.11	2.80	3.67	-7.8453	-1.2476	-0.9016	0.2734	-0.0392	0.0280
		1	1.38	2.54	3.12	-6.0406	-2.6215	-1.3062	0.2663	-0.2050	0.1599
		2	3.09	32.58	30.83	1.7225	3.1083	0.9207	0.2519	0.2946	0.1898
		So_1	0.58	1.48	1.72	-0.0374	-0.0024	0.0041	0.0029	-0.0009	-0.0004
		So_2	16.48	18.18	25.99	-0.0165	-0.007	-0.0025	0.0000	0.0001	-0.001

Table 2: A_i Results for L_i, N_a, K, C_a, and Z_n atoms

[L_i]

L	A_1	A_2	A_3	A_4	A_5	A_6
0	78.07395	-109.36503	51.71981	0.57288	-0.28227	-0.27460
1	47.21382	-16.76466	-2.56942	-2.32355	-0.17881	0.05299
2	43.20601	-29.38373	6.05858	-129180	-0.34902	0.02958

[NA]

L	A_1	A_2	A_3	A_4	A_5	A_6
0	44.66191	-66.21326	37.29997	0.19264	-0.49985	-0.20105
1	27.79250	-4.57524	-1.28774	-2.32245	0.47952	-0.04965
2	11.06046	-66.21326	37.29997	0.19264	0.49985	-0.06744

[K]

L	A_1	A_2	A_3	A_4	A_5	A_6
0	51.65715	-75.47792	43.03156	0.37112	-0.35745	-0.20105
1	34.15055	-5.67858	-2.61607	-2.60972	-0.49116	-0.04965
2	14.15523	5.48528	-1.20937	-1.23555	-0.17929	0.06744

[Zn]

L	A_1	A_2	A_3	A_4	A_5	A_6
0	66.03779	-123.17795	99.83706	-2.82897	0.35245	0.03456
1	10.29377	70.43324	-14.06683	0.13694	25.34715	9.25869
2	3.27978	-806.42524	732.50003	-5.32135	121.38282	-124.84925
So_1	-123.17795	99.83706	-2.82897	0.35254	-0.34565	1.75000
So_2	70.43324	-41.06683	0.13694	25.34715	9.25869	1.2500

5. LIQUID METAL RESISTIVITY

The electrical resistivity of liquid transitional metals is given by the Ziman's formula (Ziman 1961). Where Ω_o 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 from equ (8). The model potential parameters developed by Animalu and Heine (1965) were used in the calculations.

Table 3: Model Potential Parmeters (Animalu,1965) Used For the Calculation of Liquid Metal Resistivity for, Lithium, Sodium Postassium, Calcium and Zinc.

Element	A_o	A_1	A_2	R_m	Ω	Z	M^*	K_f	$(^{1/2}/W)^2$	$\frac{dA_o}{dE}$	$\frac{2dA_o}{dE}$	$\frac{dA^2}{dE}$	α
L_i	0.328	0.400	0.218	2.600	144.9	1	1.330	0.5890	0.547	0.605	1.000	1.844	0.096
Na	0.312	0.357	0.980	2.200	254.5	1	1.096	0.4882	0.201	0.187	0.117	1.802	0.087
K	0.248	0.248	0.500	0.212	481.4	1	0.884	0.3947	0.450	0.240	0.287	0.846	0.086
C_a	0.610	0.607	0218	2.600	293.5	2	1.000	0.5865	0.375	0.123	0.288	0.774	0.038
Zn	1.029	1.405	0.980	2.200	102.0	2	1.000	0.8342	0.610	0.300	0.123	0.096	0.079

In table 3, A_o, A_1, A_2 are the corresponding model potential well depths, R_m is the model radius, Ω is the atomic volume, Z in the valance charge, M* is the effective mass and K_f is the fermi wave vector.

Table 4: Experiment and Calculated Values for Liquid Metal Resistivity for Lithium, Sodium, Potassium, Calcium and Zinc (in units of ohm-cm).

Liquid metals	*Experimental values faber (1977)*	*Calculated values*
L_i	**24.0**	**23.2**
Na	**9.6**	**6.4**
K	**13.0**	**12.1**
C_a	**33.0**	**28.9**
Zn	**37.4**	**35.6**

The liquid metal resistivity of lithium, sodium, potassium calcium and zinc were computed. The results obtained are shown in table 4, where they are compared with experimentally obtained values (Faber, 1977). It is observed that the calculated results are 88% in good agreement with experimentally obtained results.

6. DISCUSSIONS AND CONCLUSION

The liquid metal resisitivty are calculated using pseudopotential form factors. The input parameters yield 88% agreement with the experimental structure factors. The C_i parameters as tabulated by Bachelet et al (1982) are shown in Table 1 for Lithium, sodium, potassium calcium and zinc together with the values of $\alpha_1,\alpha_2,\alpha_3$. These parameters were used to calculate the linear coefficient parameters A_i as well as adapting the prescription of Pattnaik et al (1979), which eliminated the numerical instability problems on the calculated A_i are shown in Table 2. The model potential derived from spectroscopic term values by Animalu and Haine (1965) are shown in Table 3. This modified form of the model potential has the advantage that it includes both a repulsive exchange overlap (core-core) part, and attractive part that takes into account s – d hybridization, and is purely columbic outside the parameric radius Rm. For screening we used the simple Thomas-fermi type of dielectric function, which is quite adequate for liquid metal resisitivity calculations to ensure that we have $-2/3E_f$ limit as q tends to zero.

We have applied the pseudopotential form factor in calculation of the liquid metal resistivity for metals and the results obtained are tabulated in table 4 where they are compared with the experimentally obtained results of Faber (1977). The results are 88% in good agreement with the experimental results.

It is interesting to note that the pseudopotential form factors 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.

The results of the pseudoptential form factor calculation provide exciting insight to many applications as proposed by Slater (1937). It is our belief that the application of the pseudopotential form factor calculations to other phenomena like phonon frequencies, optical properties etc will not be different.

We cannot conclude without pointing out a major problem encountered. During the calculation of the values of A_i for each element, we encountered a problem of zero result for quantum number, l = 2. This bottle-neck was overcome by putting a modulus in all the square root functions. The Ai's were used to carry out some checks with Nickel and Vs(q) behave as is expected in the limit as q 0 (Sattar, 2003)

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