LATTICE PSEUDO-POTENTIAL APPROACH AND HOPPING IN THE BINDING OF Zr AND Mo

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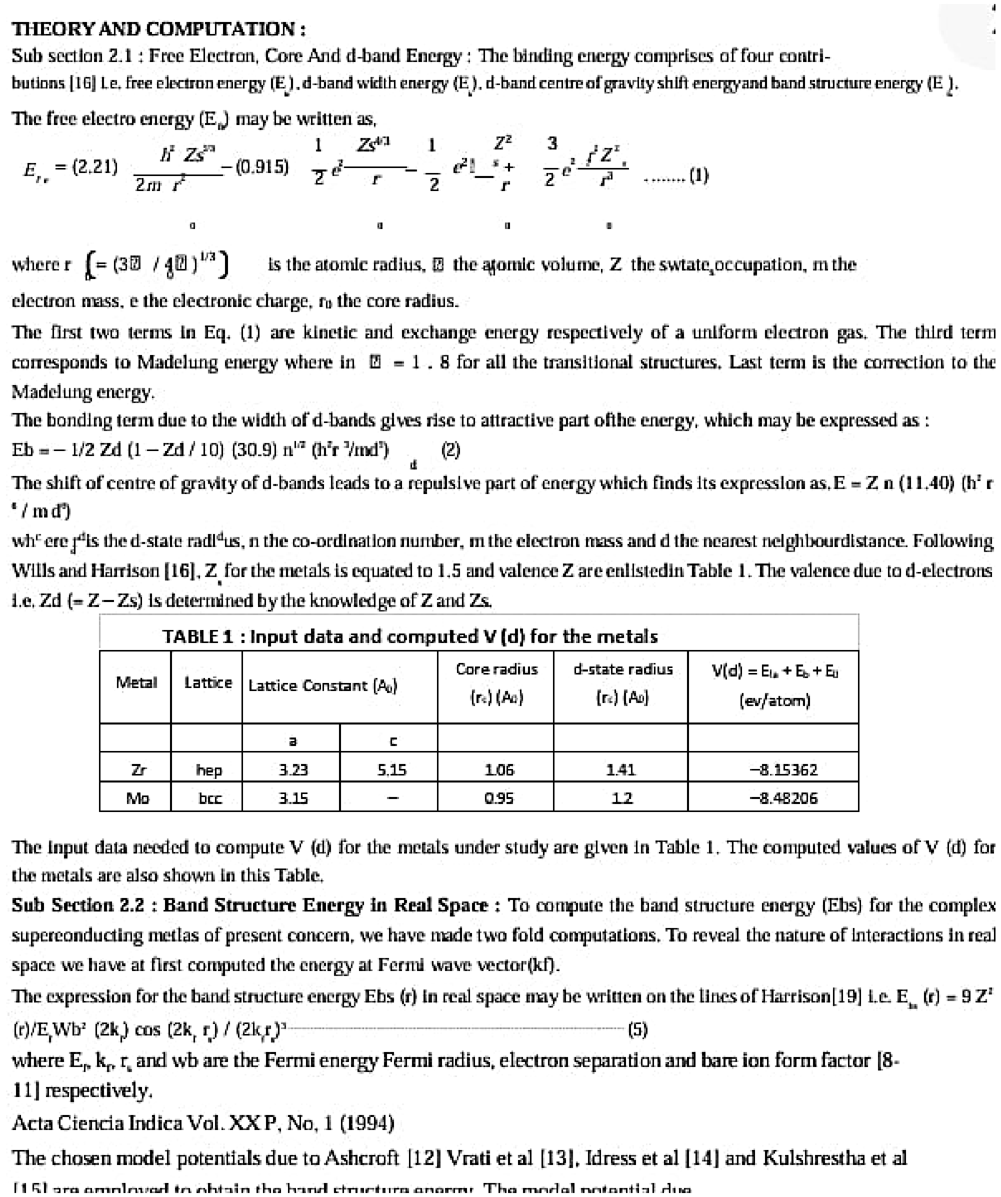
A comprehensive and through analysis of binding energy, comprising of terms due to free electron gas, core, d - bands and band structure components, is carried out for the complex metals which show superconducting properties at low temperature. The valence dependent band structure energy expressed in real nd fourier space leads to oppositely directed hybridisation. In real space the hopping of electrons, from d - bands to s - bands, gives rise to altracitve band structure energy, while the band structure energy in fourier space owes its altractive character to the hopping process from s - bands to d-bands.

The total biding energy computed for the metals agrees satisfactorily with experimental data.

1. **INTRODUCTION** : Atomic sphere approximation and muffin-tin orbital theory have been employed by Pettifor [1], Anderson [2] and Mruzzi et al [3] to propound the role played by the s and d electrons in the bonding of complex metals. Wills and Harrison [4] have dealt with the s-s interactions while Harrison and Froyen [5] have formulated the interactions implicating the d-band electrons. Helikowsky [6] has calculated the binding energy of simple metals in Thomas Fermi approximation. Empty core potential due to Heine and Abarenkov [7] has been deployed by Singh et al [8] while Wills and Harrison [4] have used a similar potential due to Ashcroft [12] to calculate the binding in metals. These potentials [7-12] beside discontinuous in real space do not imbie the short range repulsive character explicitly iun their formulations.

Various interactions energy associated with the elelctrons are influenced by s-d hybridisation which sub- stantially alters the effective occupancy of metallic d and s-states. The phenomenon of electron screening also contribute to the binding of the metals.

The binding in metals provides a basic genesis to discuss the cohesive, elastic, lattice dynamical and other allied properties of metals. A through and compprehensive analysis with regards to (i) various energy terms contributing to the total metallic bonding (ii) forms of model potential incurring the band structure part of the bidning (iii) implication of s-d hybridisation and (iv) effect of electron screening, hasprompted us to undertake the present state of binding in Zirconium (Zr) and Molybdncnum (Mo) which turn out be superconducting at low temperature and bear hep & bcc configurations at room temperature. The papar is organised in three sections; second section of 'Theory and Computation' is divided in four sub section. Sub section 2.1 outlines the terms corresponding to Fermi, exchange, core, core correction, d-band width and centre shift of d-bands energy. The evaluation of these terms for the metals cited above is also given in this sub section. Sub section 2.2 deals with the computation of band structure energy in real space. The dependence of this energy on occupancy number of the electrons Z(r) is also investigated in this sub section. The computation of band structure energy in fourier space and its dependence on valence are given in this sub section 2.3. Sub section 2.4 is devoted to total sum of contributions to the binding and its comparision with the experimental data. The results and conclusions are given in the thirdsection.



THEORY AND COMPUTATION :

Sub section 2.1 : Free Electron, Core And d-band Energy : The binding energy comprises of four contributions [16] i.e. free electron energy (E), d-band width energy (E), d-band centre of gravity shift energyand band structure energy (E).

The free electro energy (E_{fe}) may be written as,

$$E_{fe} = (2.21)\frac{\hbar^2 Zs^{5/3}}{2m\, r_a^2} - (0.915)\frac{1}{2}e^2\frac{Zs^{4/3}}{r_a} - \frac{1}{2}e^2\alpha\frac{Z_s^2}{r_a} + \frac{3}{2}e^2\frac{r_c^2 Z_s^2}{r_a^3} \quad \ldots\ldots (1)$$

where r_a $\left(= (3\Omega / 4\pi)^{1/3}\right)$ is the atomic radius, Ω the atomic volume, Z_s the swtate occupation, m the electron mass, e the electronic charge, r_0 the core radius.

The first two terms in Eq. (1) are kinetic and exchange energy respectively of a uniform electron gas. The third term corresponds to Madelung energy where in α = 1 . 8 for all the transitional structures. Last term is the correction to the Madelung energy.

The bonding term due to the width of d-bands gives rise to attractive part ofthe energy, which may be expressed as :

$Eb = - 1/2\ Zd\ (1 - Zd / 10)\ (30.9)\ n^{1/2}\ (h^2 r_d^3/md^5)$ (2)

The shift of centre of gravity of d-bands leads to a repulsive part of energy which finds its expression as. $E = Z\ n\ (11.40)\ (h^2 r_d^6 / m\, d^8)$

where r_d is the d-state radius, n the co-ordination number, m the electron mass and d the nearest neighbourdistance. Following Wills and Harrison [16], Z_s for the metals is equated to 1.5 and valence Z are enlistedin Table 1. The valence due to d-electrons i.e. Zd (= Z – Zs) is determined by the knowledge of Z and Zs.

TABLE 1 : Input data and computed V (d) for the metals

Metal	Lattice	Lattice Constant (A_0)		Core radius (r_c) (A_0)	d-state radius (r_d) (A_0)	$V(d) = E_{fe} + E_b + E_{cl}$ (ev/atom)
		a	c			
Zr	hcp	3.23	5.15	1.06	1.41	–8.15362
Mo	bcc	3.15	–	0.95	1.2	–8.48206

The input data needed to compute V (d) for the metals under study are given in Table 1. The computed values of V (d) for the metals are also shown in this Table.

Sub Section 2.2 : Band Structure Energy in Real Space : To compute the band structure energy (Ebs) for the complex supereconducting metlas of present concern, we have made two fold computations. To reveal the nature of interactions in real space we have at first computed the energy at Fermi wave vector(kf).

The expression for the band structure energy Ebs (r) in real space may be written on the lines of Harrison[19] i.e. $E_{bs}(r) = 9Z^2(r)/E_f Wb^2(2k_f)\cos(2k_f r_s)/(2k_f r_s)^3$ ………………………… (5)

where E_f, k_f, r_s and wb are the Fermi energy Fermi radius, electron separation and bare ion form factor [8-11] respectively.

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The chosen model potentials due to Ashcroft [12] Vrati et al [13], Idress et al [14] and Kulshrestha et al [15] are employed to obtain the band structure energy. The model potential due

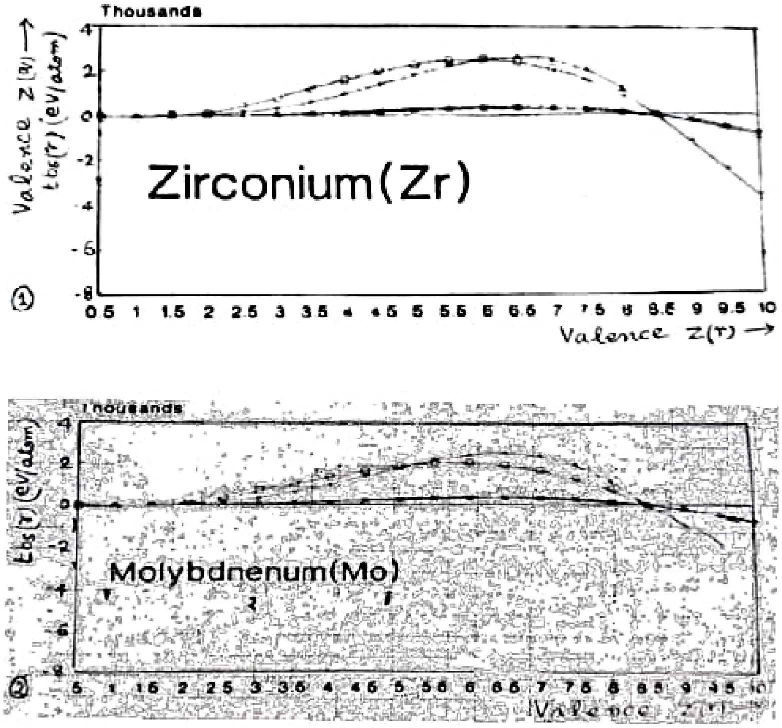
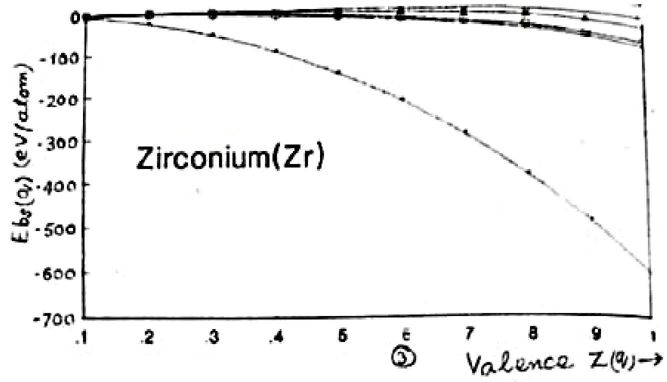


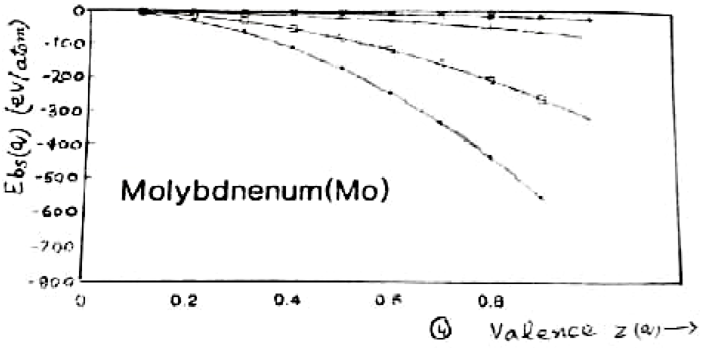
Fig. : 1 & 2 show the dependence of structure Energy Ebs (r) on valence Z (r) to the Ziroconium and Molydenum, in real space.
Markings [+, *,]. in figs. 1.2, represent the computed findings for the Model potentials due to Ashcroft [12], Vrati et al [13], Idreas et al [14] and Kulshrestha et at [15] respectively.

TABLE 2 : Input data to computed E_{bs} (r) E_{bs} (q) for the metals

Metal	Atomic volume ( ) 10^{-24} cm^{-1}	Fermi wave vector (k_f) 10 cm^{-1} 5	Atomic radius (Rc) (A°)	Ionic radius (Ri) (A°)	Wingner-Seitz radius (R_0)
Zr	23.2655	1.0829	1.44	0.78	1.77
Mo	15.6279	1.2387	1.29	0.62	1.55

to Ashcroft [12], a most commonly used negative core potential ingnores the explicit inclusion repulsivecharacter whereas the other potentials [13-15] accounts for the repulsive part in their own characterstic manner. The input data needed to compute the E_{bs} (r) are given in Table 2.





Figs. 3& 4 show the depdence of Band structure energy Ebc (1) on valence Z (q) to Zirconium and Molybdenum, in fourier space.

Markings [+, *,] in Figs 3 & 4, represent the computed findings for the Model potentials due to Ashcroft [12], Vrati et al [13], Idress ct al [14] and Kulshrestha et al [15] respectively.

In order to investigate the phenomenon of hybridisation the dependence of Ebs (r) on Z (r) is explored. The variation of Ebs with Z (r) is depicted in figures 1 & 2 for the metals of present concern. Relevant valence Z (r) for which the E_{bs} (r) assume the appropriately attractive character or different model potentials are enlisted in table 3.

Sub section 2.3 : Band Structure Energy is Fourier Space : For analysing the characteristic features of interactions associated with the E_{bs} (q) we have further computed the band structure energy in fourier space which may be expressed as :

$E_{bs}(q) = !_0 / (4pe^2)$ ▯ $q^2 W_b^2(q)$ ¢ $(q) - 1) / (1 + \{\text{epsilon}\,(q) - 1(1 - f(q))\})$ ....(6)

TABLE 3 : Appropriate E_{bs} (r) and Z (r) for the model potential due to [12-15]

Model Potential	Zr		Mo	
	Valence	E_{bs} (r) (ev / atom)	Valence	E_{bs} (r) (ev / atom)
Ashcroft [12]	8.570	−11.3271	8.530	−13.30289
Vrati et al [14]	8.562	−11.3121	8.521	−12.88550
Idress et al [14]	8.542	−11.56397	8.496	−13.33284
Kulshrestha et al [15]	8.544	−12.5586	8.500	−13.23612

Where ▯ (q) the usual Hartree-Fock dielectic function, f(q) the correction factor due to exchange and correlation effect associated with the electrons and W_b(q) the bare ion form factor [8–11].

Present investigation employs and efficient and moderate scheme due to Vashista and Singwi [18] for computing f(q).

In oreder to study the process of s-d hydridisation the E_{bs} (q) are computed for different Z(q). The com- puted plots E_{bs}(q) Vs Z(q) within the frame work of the said potentials are shown in Figures 3&4. Table 4 exhibits some of the appropriate and attractive computed values of Ebs (a) with the corresponding appro-priate valcnee Z(q).

TABLE 4 : Appropriate E_{bs} (q) and Z (q) for the model potential due to [12-15]

Model Potential	Zr		Mo	
	Valence Z (q)	E_{bs} (q) (ev / atom)	Valence Z (q)	E_{bs} (q) (ev / atom)
Ashcroft [12]	8.410	−11.90632	8.411	−13.14206
Vrati et al [13]	8.747	−11.98603	8.730	−13.11701
Idress et al [14]	8.141	−11.89693	8.138	−13.03255
Kulshrestha et al [15]	8.450	−11.93200	8.200	−12.96980

Sub Section 2.4 : Total binding Energy : The total binding energy for the metallic ions of given valence and occupying the finite volume within the quoted model potentials treated in second order may be written as,

Ebind = V(d) + E_{bs} (r or q) .... (7)

For computing the binding energy in real space we have substitued the E_{bs}(r) at Z(r) as per contents of the Table 3.

The binding energy in fourier space is computed by putting the E_{bs} (q) AT Z(q) obtained from thedata given in Table 4.

Ebind (Experimental) = –Ecohesive – Er –1/4 (E_I + E_{II})

TABLE 5 : Appropriate E_{bs} (q) and Z (q) for the model potential due to [12-15]

Model potential	Zr	Mo
Ashcroft [12]	−19.5685	−21.7848
Vrati et al [13]	−19.5658	−21.1617
Idress et al [14]	−19.7176	−21.8148
Kulshrestha et al [15]	−19.7123	−21.7181

TABLE 6 :Total binding energy E_{bind} (ev/atom), obtained by using E_{bs} (q) in fourier space.

Model potential	Zr	Mo
Ashcroft [12]	−20.0599	−21.6241
Vrati et al [13]	−20.1496	−21.6090
Idress et al [14]	−20.0505	−21.5146
Kulshrestha et al [15]	−20.0599	−21.4518

Where Ecohesive is the cohesive energy, E1, the first inonisation energy and EII the second ionisation energy. The Ecohesive, E1 and EII data are taken from kittel [17].

3. **Result and Discussion :** Present investigation accounts comprehensively for the contributions of almost all interactions present in the metals. The theory besides being extensive as compared to others [6, 10, 15] predicts good agreement with the experimental values. The study establishes that all the chosen model potentials irrespective of their shapes and theoretical details lead to almost identical predictions of valence correlated band structure bonding.

The valence dependence of $E_{bs}(r)$ [Figs. (1–6] exhibits one type of hydridisation which suggests hopping of electrons from d-bands to s-bands. the $E_{bs}(q)$ Vs Z(q) [Figs. (7–12)]

Study reveals other type of hydridisation associated with unscreened and screened electron-ion interac- tions points toward the inverse correlation between valence and shift of interaction energy due to the pseudo potential. The correlation may be attributed to the degree of oscillations of electron wave function occuring inside the core region.

The hopping procesds, emerging out of the present investigation, have important bearing on the theory attempting to explain the hot super conduction.

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