# A comparative study of two different embedding functions

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## We examine the electron density obtained from two embedding functions, regarded as model I and model II, from the Separable Potential Method for six FCC metals; Ni, Cu, Pd, Pt, Au and Ag. The purpose is to investigate whether a unique electron density could be obtained from the two functions using Johnson's alloy model. Experimental dilute limit heats of solution of the binary alloys of these metals were used as input parameters. The embedding functions are essentially the same for the two models from $\rho$ = 0 up to $\rho = 5\rho_{e}$ for Ni, Cu and Ag. The functions diverge from about $1.3\rho_{e}$ upwards for Pd and from about $1.8\rho_e$ upwards for Pt and Au. The equilibrium electron density, $\rho_e$ , was taken as $k/\Omega$ , where k is an integer and $\boldsymbol{\Omega}$ is the atomic volume. Two different electron densities were derived from each model for k < 30 but at higher values of k the two electron densities became identical. The lower electron density in each case was found to increase linearly with k. Though the two embedding functions were identical in some density regions, the observed differences between them may be the reason for non-uniqueness of the electron densities derived from them.

*Keywords*: Analytic Electron Density, Embedded Atom Method, Semi-Empirical Methods.

# 1.0 Introduction

An appealing aspect of EAM is that each atom is embedded in a host of electron gas created by its neighboring atoms. Thus, the same embedding function is used to calculate the energy of an atom in an alloy and in the pure material. To apply this method to the study of pure metals, surface defects, alloy energetic and allied defects, atomic densities which could be taken from Hartree-Fock calculations or some other source are usually required as input. Also some form of embedding function will have to be assumed. While these provide sufficient information about the embedding function for many calculations in pure metals, the atoms in an alloy are embedded in electron densities that are substantially different from that in pure metals [1]. One ambiguity that may arise in using these electron densities is that the electronic configuration in a free atom may not be the best representation of the electron density in the pure monoatomic solid or in an alloy.

An attempt to solve this problem gave rise to Johnson's analytical model in which simple exponential functions are employed for both the electron density,  $\rho(r)$ , and the two-body potential  $\phi(r)$  [2]. The embedding function is thereby determined simply by fitting these functions to the universal equation of state [3].

However, the theoretical predictions for the dilute limit heats of solution for the binary alloys of six FCC metals using Johnson's model showed a significant disagreement from the experimental values, especially in the case of Palladium. Besides, the atomic density parameter in Johnson's equation can only be determined from alloy properties [4]. The problem before us is therefore to determine the electron density function and the two-body potential function that will yield the correct dilute limit heat of solution

The search for an appropriate electron density is partly responsible for this study. In this work, we examine the electron densities arising from two different embedding functions derived from the Separable Potential Method (SPM), [4] and we inquire whether a unique electron density could be obtained from the two different functions. Electron densities derived from identical embedding functions are not expected to differ. Hence, the parameters in the two embedding functions were carefully chosen so that the two functions are identical as far as possible, beginning from  $\rho = 0$ . First, the relevant EAM theory and equations are reviewed in section 2. Rather than propose analytic expressions for calculation of dilute limit heat of solution, we set out to find expressions for  $\rho(r)$  from the experimental values of heat of solution. Results and discussion of our findings are presented in section 3 and concluding remarks in section 4.

## 2.0 Theory

Daw and Baskes [5] originally evolved the EAM theory, and its basic ideas can be interpreted in the framework of density-functional theory as developed by Hohenberg and Kohn [6]. The significant contribution of Baskes *et al*, is that they have used the basic ideas of density functional theory to write out the total internal energy for the collection of atoms constituting the metallic solid, as an embedding energy plus a core-core repulsive potential that can be fully determined by experimental data. The electron density in the vicinity of each atom can then be expressed as a sum of the density of the atom in question plus the electron density from surrounding atoms [1]. Hence, the total energy for a monoatomic solid is given as

$$E_{tot} = \sum_{i} F_i \left( \rho(r_{ij}) \right) + \frac{1}{2} \sum_{i \in (i, j, j)} \varphi(r_{ij})$$

$$\tag{2.1}$$

 $F_i(\rho(r_{ij}))$  is the embedding energy as a <sup>*i*</sup>function of backgrbund electron density  $\rho$ .  $\phi(r_{ij})$  is the core-core repulsion between atoms i and j separated by distance  $r_{i,j}$ . The electron density  $\rho$  at an impurity site due to the contribution from neighboring host atoms is

$$\rho = \sum_{n} \rho_n(r_{h,i}) \tag{2.2}$$

The subscripts h and i refer to the host and impurity atoms respectively. The summation over n in Equation (2.2) refers to the number of the neighboring atoms at some interatomic separation distance,  $r_{(h,i)}$ , from the impurity atom, each of these neighboring atoms contributing the same density  $\rho_n(r_{h,i})$ .

There are three fundamental quantities in Equations (2.1) and (2.2). These are the embedding energy function,  $F_i(\rho(r_{ij}))$ , the electron density function,  $\rho(r_{ij})$  and the pair potential,  $\phi(r_{ij})$ . Idiodi and Obodi [4], have derived two embedding functions for FCC metals from the Separable Potential Method as.

$$F(\rho) = F(\rho_e) \left(\frac{\rho}{\rho_e}\right)^{\lambda_G} e^{-\alpha_G \left(\frac{\rho}{\rho_e} - 1\right)}; \quad \text{Model I}$$
(2.3)

$$F(\rho) = -\left[f\left\{e^{\alpha_{f}} - e^{-\alpha_{f}\left(\frac{\rho}{\rho_{e}} - l\right)}\right\}\right]^{\lambda_{f}} \qquad \text{ModelII}$$
(2.4)

Following Johnson [2], the relevant equation for the dilute limit heat of solution,  $\Delta Q$ , of an impurity atom in a host metal is given by

$$\Delta Q = -F_h(\rho) - 12\varphi_{hh} + F_i(\rho) + 12\varphi_{hi} - 12F_h(\rho) + 12F_h(\Delta\rho) - E_h + E_i$$
(2.5a)

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$$\Delta \rho = \frac{\rho_h + \rho_i}{12} \tag{2.5b}$$

$$\varphi_{hh}(r_h) = \frac{1}{6} \left( E_h - F_h(\rho_{eh}) \right)$$
(2.5c)

$$\varphi_{ii}(r_i) = \frac{1}{6} \left( E_i - F_i(\rho_{e_i}) \right)$$
(2.5d)

$$\varphi_{ii}(r_h) = \frac{1}{6} \left( -E_i \left( 1 + \alpha \left( \frac{r_h}{r_i} - 1 \right) \right) e^{-\alpha \left( \frac{r_h}{r_i} - 1 \right)} - F_i(\rho_{e_i}) \right)$$
(2.5e)

$$\varphi_{hi}(r_h) = \frac{1}{2} \left( \frac{\rho_i}{\rho_h} \varphi_{hh}(r_h) - \frac{\rho_h}{\rho_i} \varphi_{ii}(r_i) \right)$$
(2.5f)

The only unknown in the full expression for equation (2.5a) is the electron density,  $\rho_i$ . This quantity is obtained by iterating the expression, (2.5a), in order to reproduce the exact heat of solution for each combination of impurity/host atom as presented in Table 2.1. Other material properties of the FCC pure metals used as input for the calculation are given in Table 2.2.

 Table 2.1. Experimental heats of solution [in eV] of binary alloys of Cu, Ag, Au, Ni, Pd and Pt. Unrelaxed values from

 [1], denoted with superscript a, are used where experimental values are not available.

			Impurity							
		Ni	Cu	Pd	Pt	Au	Ag			
	Ni		0.11	0.06	-0.28	0.28 <sup><i>a</i></sup>	0.42 <sup>a</sup>			
	Cu	0.03		-0.44	-0.53	-0.19	0.39			
st	Pd	-0.09	-0.39		$-0.04^{a}$	-0.2	-0.11			
Hc	Pt	-0.33	-0.30	$-0.03^{a}$		$0.07^{a}$	$0.18^{a}$			
	Au	0.22	-0.13	-0.36	$0.09^{a}$		-0.16			
	Ag	$0.38^{a}$	0.25	-0.29	$0.07^{a}$	-0.19				

<sup>*a*</sup>see ref. [1]

**Table 2.2**: Properties of pure FCC metals. Lattice constants (in Å), Bulk modulus ( in 10<sup>12</sup>ergs/*cm*<sup>3</sup>), and cohesive energies (in eV) are from Ref. [3] and Ref. [1], elastic constants (in 10<sup>12</sup>ergs/*cm*<sup>3</sup>).

	Ni	Cu	Pd	Pt	Au	Ag
B[10 <sup>12</sup> ergs/cm <sup>3</sup> ]	1.804	1.380	1.950	2.830	1.670	1.040
$C_1[10^{12} ergs/cm^3]$	2.465	1.700	2.341	3.470	1.860	1.240
$C_{\Box\Box}\Box$ [10 <sup>12</sup> ergs/cm <sup>3</sup> ]	1.473	1.225	1.760	2.510	1.570	0.934
$C_{44}[10^{12} ergs/cm^3]$	1.247	0.758	0.712	0.765	0.420	0.461
<i>a</i> (Å)	3.520	3.615	3.890	3.910	4.080	4.090
$\Omega\square(\text{\AA}^3)[=a^3/4]$	10.9036	11.8104	14.7160	14.9441	16.9793	17.1045

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$r_e(\text{\AA})[=a/\sqrt{2}]$	2.4890	2.5562	2.7506	2.7648	2.8850	2.8921
$E_c[eV]$	4.45	3.54	3.91	5.77	3.93	2.85

## 3.0 Results and discussions

The input parameters for EAM calculations for the Six FCC metals are presented in Table 3.1.Forthese calculations, and  $F(\rho_e)$ , f,  $\alpha$ ,  $\lambda_f$  and  $\lambda_G$  were taken from [4]. To examine the sensitivity and to reconcile our calculations with earlier studies [4,8],  $\rho$  was simply taken as  $k/\Omega$ , where k was increased from 1 to 200. Calculated electron densities at k=1 are shown in Table 4. Calculations show that  $\rho$  is sensitive to the choice of k. Generally below k = 30, there are two values for each impurity at k = 1, which are regarded here as upper and the lower roots. The two roots generally converge as from k ~ 40. It is noted here that the lower root scales linearly with k as can be seen in Figure 1 for Cu.

The results of electron densities (lower roots for the two models), are plotted in Figure 2 for k = 1 for all six elements. Electron densities derived from the two embedding functions are surprisingly different without exception. The curves do not seem to indicate any specific functional form and can hardly be fitted with some exponential functions. We remark here that two instabilities were noted during the calculations with Cu impurity in Ni and Ag impurity in Pt.

For embedding function calculations in pure metals, small changes in  $\rho_e$ , less than  $\pm 10\%$ , can be sufficiently estimated by a harmonic approximation [7]. This is often inadequate for most defect calculations, which require a wider range. Certainly, a better approximation of electron density is obtained from alloy calculations. Thus, we have calculated the embedding functions up to  $10\rho_e$  for models I and II as shown in Figure 3 for the six FCC metals. The calculated embedding functions are essentially the same for the two models up to  $5\rho_e$  for Ni, Cu and Ag. This is likely due to the fact that they are derived from the same atomic cluster arrangement. The functions diverge from about  $1.3\rho_e$  for Pd and at about  $1.8\rho_e$  for Pt and Au. For all the six metals, embedding functions arising from model I show a positive curvature even up to  $10\rho_e$ . It is desirable that  $F''(\rho) > 0$  for all  $\rho$ . We remark here that the expressions for  $F(\rho)$  were taken from [4].

Perhaps, it is noteworthy to mention that the embedding function from model I consistently gave electron density that is comparable to published results [8]. Why that of Equation (2.4) gave extraordinarily high electron densities especially in Pd host is a subject for further investigation.

	Ni	Cu	Pd	Pt	Au	Ag
$\rho_0 = \rho(\Box r_0)_\Box \Box [\text{Å}^{-3}]$	0.0917	0.0847	0.0680	0.0669	0.0589	0.0585
$\rho'(r_{\square})[\rho_0/{\mathring{A}}]$	-0.0861	-0.1340	-0.1599	-0.1465	-0.1333	-0.1149
$\rho^{\prime\prime}(r_{\Box})[\rho_0/\AA^2]$	0.1261	0.0819	1.0074	0.2951	0.6381	0.0494
$F(\rho_0)[eV]$	-8.7025	-7.3643	-3.9234	-9.0164	-4.8356	-6.1665
$F'(\rho_0)[eV/\square\rho_0]$	-62.626	-59.56075	-18.955	-68.368	-28.77	-74.50739
$F''(\rho_0)[eV/{\Box}{\rho_0}^2]$	301.281	264.24996	447.782	892.922	741.266	411.33117
$\Box \Box \phi(eV)$	0.7088	0.6374	0.0022	0.5411	0.1509	0.5528
$\phi'[eV/\mathring{A}]$	-0.8989	-1.3297	-0.5052	-1.6693	-0.6393	-1.4272

**Table 3.1:** Calculated EAM parameters for Six FCC metals.  $\rho_0$  is simply taken as the inverse of the atomic volume and  $F(\rho_0), f_1, \alpha$ , and  $\lambda$  were taken from [4].

$\phi''[eV/\AA^2)$	3.9159	2.3581	4.8250	5.3489	4.0527	1.6995
$V_{11}[\rho_0]$	-0.0714	-0.1141	-0.1466	-0.1350	-0.1282	-0.1108
$W_{\Box\Box}\Box[\rho_0]$	-0.0382	-0.0429	0.8488	0.1535	0.6893	-0.0407
$W_{\Box 2}[\rho_0]$	0.0585	0.1043	0.4406	0.2289	0.3711	0.1077
α	4.9829	5.0855	6.4208	6.4166	6.3663	5.9213

	Ni	Cu	Pd	Pt	Au	Ag
θ	0.2143	0.3424	0.4399	0.4050	0.3847	0.3324
$\alpha_{G}$	0.0668	0.0414	0.3065	0.1935	0.3041	0.0206
$\lambda_{\mathrm{G}}$	0.7268	0.7262	0.6348	0.7009	0.6545	0.7270
$\alpha_{f}$	0.1905	0.1194	1.3767	0.6833	1.3121	0.0580
$\lambda_{\mathrm{f}}$	0.7273	0.7273	0.7273	0.7273	0.7273	0.7273
f	93.3412	122.7647	2.2118	20.9773	3.2177	204.2780

**Table: 3.2** Calculated electron densities  $\rho(r)$  for the six FCC metals for the two models. Equilibrium electron density for each host metal is simply taken as  $k/\Omega$ , where k = 1.

Model I						
<b>r</b> (Å)	Ni1	Cu1	Pd1	Pt1	Au1	Ag1
2.489016	0.09171	2.333708	0.025883	0.020852	0.003293	0.006552
2.556191	0.083402	0.08467	0.034901	0.031699	0.011787	0.017694
2.750645	0 047099	0.041652	0.06795	0.060152	0 034194	0.038194
2.764788	0.041585	0.041792	0.059642	0.06602	0.039785	0.884774
2.884996	0.041104	0.02706	0.037042	0.00092	0.059705	0.04596
2.892067	0.041194	0.03790	0.041283	0.051295	0.0589	0.04380
	0.042123	0.044103	0.040/13	0.051285	0.041672	0.05846
Model II						
r (Å)	Ni2	Cu2	Pd2	Pt2	Au2	Ag2
2.489016	0.09171	2.288085	0.024975	0.020596	0.002811	0.006549
2.556191	0.083399	0.08467	0.135157	0.108821	0.13932	0.094282
2.750645	0.076508	0.078317	0.06795	0.068595	0.079681	0.07133
2.764788	0.080573	0.075904	0.068542	0.06692	0.069538	0.06616
2.884996	0.06956	0.070741	0.10213	0.060432	0.0589	0.061253

# 4.0 Conclusion

Generally the calculated embedding functions,  $F(\rho)$ , from models I and II appear to be the same for all the six FCC metals, from  $\rho = 0$  to  $1.8\rho_e$ . This is likely due to the fact that they are derived from the same atomic cluster arrangement. Perhaps, it is noteworthy to mention that the embedding function from model I consistently gave electron densities that are comparable to published results. Two different electron densities were derived from each model for k < 30. The lower roots were found to scale linearly with k.  $\rho$  is sensitive to k and above  $k \sim 30$ , the two roots from each embedding function became identical. Electron densities derived from identical embedding functions are not expected to differ.

Though the two embedding functions were identical in some density regions, the observed differences may be the reason for non-uniqueness of the electron densities derived from them. This surely raises several questions. How transferable are the electron densities obtained in this study? Are the densities of relevance in a different experimental situation? Given the sensitivity of the electron density to the form of the embedding function, what is the correct form of the embedding function? These questions are currently under the investigation and the outcome of our studies will be reported in the future.

(a)

(b)



Figure 1: Electron density versus atomic distance for Model I : higher roots and ------ lower roots.



Figure 2:- Electron density versus k for Cu using model I: lower roots, ◊ higher roots. The plot is typical of all the six FCC metals.



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