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***Ab initio* pair potentials for FCC metals: an application of the method of Möbius transformation**

Abhijit Mookerjee†, Nan-xian Chen‡, Vijay Kumar§ and Mohammad Abdus Satter¶

International Centre for Theoretical Physics, PO Box 586, 34100 Trieste, Italy

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Abstract. We use the method of Möbius transformation introduced by Chen to obtain pair potentials for FCC metals from first-principles total energy calculations. The derivation is exact for radial potentials and it converges much faster than the earlier reported method of Carlsson–Gelatt–Ehrenreich. We have tested this formulation for Cu using the tight binding representation of the linear muffin-tin orbital method. Our results agree with those obtained by Carlsson and co-workers and qualitatively with the other Morse-type pair potentials derived from effective medium theories.

1. Introduction

Of the various approaches which describe the interatomic interactions in condensed matter, one of the physically more appealing is the idea of *pair potentials*. Formally, the pair potential $\Phi(R)$ may be defined from the cohesive energy per atom E_{coh} by the relation

$$E_{\text{coh}} = \frac{1}{2} \sum_{R \neq 0}^{\infty} \Phi(|R|). \quad (1)$$

For most applications the pair potential is considered to be spherically symmetric and in various situations either the Lennard-Jones form is extensively used (see Abraham (1984) and the references therein) as in Van der Waals solids, or various generalisations of the Morse-type potentials are used for metals (Johnson (1988) and the references therein).

In general there is no reason whatsoever for assuming that the cohesive energy can be written in the form (1). Certainly we cannot prove that it can be so. In fact, there are attempts now to include three and many-body potentials in the cohesive energy expression (see articles in Vitek and Srolovity (1989) and Nieminen *et al* (1990)).

† Permanent address: S N Bose National Centre for Basic Sciences, DB17, Sector 1, Salt Lake City, Calcutta 700064, India.

‡ Permanent address: Institute of Applied Physics, Beijing University of Science and Technology, Beijing 100083, China and CCAST (World Laboratory) POB 8730 Beijing 100080, People's Republic of China.

§ On leave from Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, 603102, India.

¶ Permanent address: Department of Physics, University of Dhaka, Dhaka-1000, Dhaka, Bangladesh.

However, if we wish to think of cohesion in solids in terms of chemical bonding between the pair of atoms constituting it, the *ansatz* is an appealing one. The simplicity of pair potentials has made it possible to study the mechanical and defect properties of metals on one hand, while for the description of the phase diagram of binary alloys, this *ansatz* reduces the statistical mechanical problem to one closely resembling the para- to antiferro-magnetic phase transition problem. The pair potentials then relate to the pair interaction between magnetic moments. In recent years efforts have been made to obtain *pair interaction energies* from *ab initio* calculations (see Ferreira *et al* (1991) and references therein). However, in general such interaction energies are calculated considering only the nearest-neighbour interactions. One of the earlier successful attempts to obtain the pair potentials from first-principles band structure total energy calculations was carried out by Carlsson *et al* (1980). However, the convergence of the pair potential for their method is quite slow. Recently Chen (1990) and Chen and Ren (1991) have suggested a new method of inverting the cohesive energy to obtain pair potentials using the Möbius transformation. The resulting equations converge much more rapidly than through the procedure of Carlsson *et al* (1980). In this paper we apply this procedure to FCC metals and calculate an *ab initio* pair potential for copper. For the calculation of the cohesive energies we have used the tight binding representation of the linear muffin-tin orbital (TB-LMTO) method (Andersen and Jepsen (1984), Andersen *et al* (1985)). Our results agree in general with the *ab initio* potential obtained by Carlsson *et al* (1980) and qualitatively with the Morse-type potential obtained by Johnson (1989) using the embedded-atom method (Daw and Baskes (1983)).

In section 2, we give a brief description of the inversion procedure of Carlsson *et al* (1980) and then present our method of pair potential calculation for FCC metals. Our results for copper are presented in section 3.

2. Methodology

Band structure calculations yield the total energy, $E_{\text{tot}}(r)$, as a function of the lattice constant r . The cohesive energy is then $E_{\text{coh}}(r) = E_{\text{tot}}(r) - E_{\text{tot}}(\infty)$. The interatomic separation $|\mathbf{R}_i - \mathbf{R}_j|$ may be written in terms of the lattice constant r as $S_p r$ for the p th shell of neighbours. Assuming spherical symmetry of the pair potentials, each term at a fixed value of $S_p r$ occurs with a given weight W_p in the sum in (1). These pairs of values $\{S_p, W_p\}$ are specific to a given lattice and may be easily generated for different lattices.

Thus we may write (1) as

$$E_{\text{coh}}(r) = \sum_{p=1}^{\infty} W_p \Phi(S_p r). \quad (2)$$

Now define an operator \mathfrak{R} such that

$$E_{\text{coh}}(r) = \mathfrak{R}\Phi(r) = \left(\sum_{p=1}^{\infty} \mathfrak{R}_p \right) \Phi(r) \quad (3)$$

where the operator \mathfrak{R}_p is defined by

$$\mathfrak{R}_p f(r) = W_p f(S_p r). \quad (4)$$

The formal inversion is then (henceforth we drop the subscript *coh* for simplicity)

$$\Phi(r) = \mathfrak{R}^{-1} E(r). \tag{5}$$

Carlsson and co-workers define \mathfrak{R}^{-1} as

$$\mathfrak{R}^{-1} = \left(I + \mathfrak{R}_1^{-1} \sum_{p=2}^{\infty} \mathfrak{R}_p \right)^{-1} \mathfrak{R}_1^{-1} \tag{6}$$

so that using (4) we can write (5) as

$$\begin{aligned} \Phi(r) = & \left(\frac{1}{W_1} \right) E\left(\frac{r}{S_1} \right) - \sum_{p=2}^{\infty} \left(\frac{W_p}{W_1^2} \right) E\left(\frac{S_p r}{S_1^2} \right) \\ & + \sum_{p=2}^{\infty} \sum_{q=2}^{\infty} \left(\frac{W_p W_q}{W_1^3} \right) E\left(\frac{S_p S_q r}{S_1^3} \right) - \dots \end{aligned} \tag{7}$$

This series is a very slowly convergent one (since the cohesive energy terms decrease slowly) and requires a large amount of computation effort to obtain reasonable convergence. We shall illustrate an alternative method, first suggested by one of us (Chen (1990)). The main generalisation involves the use of a renormalised operator \mathfrak{R}_1^* instead of \mathfrak{R}_1 (as in (4)). Let us illustrate this on the face centred cubic lattice with lattice constant r .

For the FCC lattice we can write (1) in the following way:

$$\begin{aligned} E(r) = & \sum_{s=1}^{\infty} 3\Phi(sr) + \sum_{s=1}^{\infty} \sum_{t=1}^{\infty} 6[\Phi(\sqrt{s^2 + t^2}r) + \Phi(\sqrt{(s-1/2)^2 + (t-1/2)^2}r)] \\ & + \sum_{s=1}^{\infty} \sum_{t=1}^{\infty} \sum_{u=1}^{\infty} [4\Phi(\sqrt{s^2 + t^2 + u^2}r) \\ & + 12\Phi(\sqrt{(s-1/2)^2 + (t-1/2)^2 + u^2}r)]. \end{aligned} \tag{8}$$

Here, the first term comes from the points lying along the axes. The 6 different directions give a weight of $(6/2)=3$. The first expression of the second term arises from the points on the cube edges lying on the coordinate planes, while the second expression arises from the points on these planes that lie on the face centres. Each of these contributions has a weight of $(12/2)=6$. The first expression in the last term arises from the points on the cube edges away from the coordinate planes. Each carries its appropriate weight. Note, equation (8) is exact.

We shall now group together the first term and the $s = t$ expressions in the second term and rewrite this as

$$\mathfrak{R}_1^* \Phi(r) = \sum_{s=1}^{\infty} 6[\Phi(sr)/\sqrt{2}] + (1/2)\Phi(sr). \tag{9}$$

We rewrite the remaining portion of the right-hand side of (8) as

$$\begin{aligned} \mathfrak{S}\Phi(r) = & \sum_{s=1}^{\infty} \sum_{t \neq s}^{\infty} 6[\Phi(\sqrt{s^2 + t^2}r) + \Phi(\sqrt{(s-1/2)^2 + (t-1/2)^2}r)] \\ & + \sum_{s=1}^{\infty} \sum_{t=1}^{\infty} \sum_{u=1}^{\infty} [4\Phi(\sqrt{s^2 + t^2 + u^2}r) \\ & + 12\Phi(\sqrt{(s-1/2)^2 + (t-1/2)^2 + u^2}r)]. \end{aligned} \tag{10}$$

Let us now define an operator \aleph such that

$$\aleph f(r) = (1/6) \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} (-1/2)^{m-1} \mu(n) f(2^{m/2} nr). \tag{11}$$

Then

$$\begin{aligned} \aleph \aleph_1^* \Phi(r) &= \aleph \sum_{s=1}^{\infty} 6[\Phi(sr/\sqrt{2}) + (1/2)\Phi(sr)] \\ &= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} [(-1)^{m-1} (1/2)^{m-1} \mu(n) \Phi(2^{(m-1)/2} n sr) \\ &\quad + (-1)^{m-1} (1/2)^m \mu(n) \Phi(2^{m/2} n sr)]. \end{aligned} \tag{12}$$

If we change the dummy variable in the first expression from m to $m' = m - 1$, then we note that, except for the term for $m' = 0$, every other term exactly cancels with a corresponding term in the second expression. Thus we finally have

$$\aleph \aleph_1^* \Phi(r) = \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \mu(n) \Phi(nsr). \tag{13}$$

We shall now use the inversion theorem of Möbius, an important theorem of number theory (Hardy and Wright (1979), Schroder (1986)). This states that

if

$$F(r) = \sum_{n=1}^{\infty} f(nr)$$

then

$$f(r) = \sum_{n=1}^{\infty} \mu(n) F(nr) \tag{14a}$$

and vice versa. Here $\mu(n)$ is the Möbius function defined by

$$\mu(n) = \begin{cases} 1 & \text{if } n = 1 \\ (-1)^q & \text{if } n \succ P(q) \\ 0 & \text{otherwise} \end{cases} \tag{14b}$$

Here $n \succ P(q)$ means that n is a product of q distinct prime numbers.

We note immediately that if in our definition of \aleph we choose $\mu(n)$ to be the Möbius function, then from the theorem of Möbius it immediately follows that $\aleph \aleph_1^* \Phi(r) = \Phi(r)$ and so

$$\aleph = (\aleph_1^*)^{-1}. \tag{15}$$

With this new choice of \mathfrak{R}_1^* we obtain an equation analogous to (7). However, by now we have already included within \mathfrak{R}_1^* most of the infinite set of dominant contributions. As such the series with this new choice converges much faster. Chen and Ren (1991) have illustrated this fast convergence on the square and hexagonal lattices. Compared to the procedure of Carlsson *et al* (1980) the expression for $\aleph E(r)$ is itself a fast converging series. This is because the cohesive energy converges to zero within several lattice constants and only a few terms of the infinite series suffice within required error limits. Also, due to (14b), some of the terms either do not contribute or there is a cancellation. In our calculations, we have included all contributions arising up to $r = 5.7r_e$ (where r_e is the equilibrium lattice constant) in the cohesive energy, and up to six terms in the series expansion for \mathfrak{R}^{-1} which can now be rewritten as

$$\mathfrak{R}^{-1} = [I + (\mathfrak{R}_1^*)^{-1}\mathfrak{Q}]^{-1}(\mathfrak{R}_1^*)^{-1}. \tag{16}$$

Tables 1 and 2 show respectively the weights and distances used for the calculations of \aleph and \mathfrak{Q} .

Table 1. Scaling indices and weights for the FCC lattice defined in (2) for the calculation of \aleph in (11).

S_p	$6W_p$	S_p	$6W_p$
1.4142	1.00	2.0000	-0.5000
2.8284	-0.75	4.0000	-0.3750
4.2426	-1.00	5.6569	-0.1875

Table 2. Scaling indices and weights for the FCC lattice defined in (2) for the calculation of \mathfrak{Q} in (10).

S_p	W_p	S_p	W_p	S_p	W_p
1.2247	12	3.4641	4	4.6904	12
1.5811	12	3.5355	36	4.7434	60
1.7321	4	3.6056	12	4.8477	48
1.8708	24	3.6742	48	4.8990	12
2.1213	12	3.7417	24	4.9498	48
2.2361	12	3.8079	12	5.0000	12
2.3452	12	3.9370	48	5.0498	24
2.4495	12	4.0620	48	5.0990	36
2.5495	36	4.1231	24	5.1478	36
2.7386	24	4.1833	24	5.1962	16
2.9155	24	4.2426	12	5.2440	72
3.0000	12	4.3012	60	5.3385	48
3.0822	36	4.3589	12	5.3852	36
3.1623	12	4.4159	24	5.4314	36
3.2404	24	4.4721	12	5.4772	24
3.3166	12	4.5277	24	5.5227	60
3.3912	24	4.5826	24	5.6125	72
		4.6368	60		

The calculation of the cohesive energy for copper has been done using the TB-LMTO method (Andersen *et al* (1985)). In this method a tight binding Hamiltonian is obtained from first principles. This involves first the calculation of a lattice structure dependent structure function $S_{iL,jL'}$, where i and j denote the sites and $L = lm$ label the angular momentum components. In the TB representation, this function is short-ranged (effectively non-zero up to the second nearest-neighbour on the FCC lattice). Secondly, it involves the determination of the potential parameters C_{iL} and $\Delta_{iL}^{1/2}$ and overlap parameters o_{iL} and p_{iL} . C_{iL} and $\Delta_{iL}^{1/2}$ determine respectively the center and the width and hybridization of the il band. The overlap parameters are determined in a single atomic sphere alone and involve only intra-atomic characteristics. The effective first-order Hamiltonian is then given by

$$H^{(1)} = C + \Delta^{(1/2)} S \Delta^{(1/2)} = E_\nu + h. \quad (17a)$$

Here h is the expansion coefficient matrix and E_ν is the energy around which the l th orbital is expanded. To obtain better accuracy we have used for our calculations the second-order Hamiltonian, which is given as

$$H^{(2)} = H^{(1)} - h o h. \quad (17b)$$

Details of this can be found in Andersen *et al* (1985). The potential parameters for copper were calculated for each r self-consistently. We have now used the recursion method (Haydock *et al* (1972)) to obtain directly the total one-electron energy of the system. This method, given the lattice structure and a reasonably short-ranged Hamiltonian, recursively obtains a set of coefficients $\{\alpha_{k,L}, \beta_{k,L}\}$ and a set of orthogonal polynomials $\{P_{k,L}(E), Q_{k,L}(E)\}$ with which the density of states $n(E)$ and any integral of the form $\int_{-\infty}^E \varphi(E') n(E') dE'$ are estimated. The method has been described in detail by Haydock (1980) and Kelly (1980) and is particularly suited for systems lacking translational periodicity and that are also interesting from the point of view of the applications of pair potentials. The recursion is carried out up to 8 steps for a cluster having 930 atoms, and the terminator, i.e. the correction due to the remaining terms is estimated using the multiband terminator scheme of Nex (1978). The spherically symmetrized charge density is obtained from the local density of states as

$$\rho(r) = \sum_L \int_{-\infty}^{E_F} dE n(r, E) |\phi_L(r, E)|^2 \langle Y_L(\hat{r}) \rangle \quad (18)$$

where $\phi_L(r)$ is the wave function obtained by numerically solving the radial part of the effective one-electron Schrodinger equation and $\langle \rangle$ refers to averaging over the angular variables. The muffin-tin potential is obtained from the charge density during the self-consistency process by solving Poisson's equation $\nabla^2 v(r) = 4\pi\rho(r)$. We have used the Hedin and Lundqvist (1971) form for estimating the exchange-correlation energy in the local density approximation, and the Madelung repulsive term is obtained by the Ewald summation method (Fuchs (1935)) with the Ewald constant (for the FCC lattice) taken to be 0.131 eV.

3. Results and discussion

In figure 1 we show the cohesive energy of copper versus the lattice constant. The full squares show the actual calculated points which were then least-square fitted to an eight-degree polynomial. This was then used in the calculation of the pair potential. The minimum of the cohesive energy occurs at $r_e = 2.67 \text{ \AA}$ which is in good agreement with the values $\simeq 2.5 \text{ \AA}$ quoted by Johnson (1989) and $\simeq 2.6 \text{ \AA}$ quoted by Carlsson *et al* (1980). Our estimate of the cohesive energy at equilibrium is 3.49 eV. This compares well with the self-consistent augmented-spherical-wave calculation (with Ewald correction), which gives a value of $\simeq 3.66 \text{ eV}$ (see Esposito *et al* (1980)). The cohesive energy vanishes at $r/r_e = 0.77$ for the calculation reported by Carlsson *et al* (1980), while in our case this vanishes at $r/r_e = 0.73$. We seem to underestimate the cohesive energy in the small r/r_e regime for which more careful calculation in the TB-LMTO may be required. It may be noted that a more appropriate Hamiltonian would be the fully Löwdin-orthogonalized LMTO Hamiltonian (Andersen *et al* (1985)) for such calculations. Also the errors due to the atomic sphere approximation (ASA) are generally small for close packed materials. However, for the calculation of pair potentials it would be more appropriate to include the combined corrections for a better estimate of energies for different r values. While we should aim for a very careful and accurate estimation of the cohesive energy, the main idea in this communication is to introduce and illustrate the Möbius transformation method as a computationally useful method for obtaining the pair potentials from first principles. The foregoing discussion is meant to justify our method of starting from a reasonable, first-principles calculation of the cohesive energy for copper.

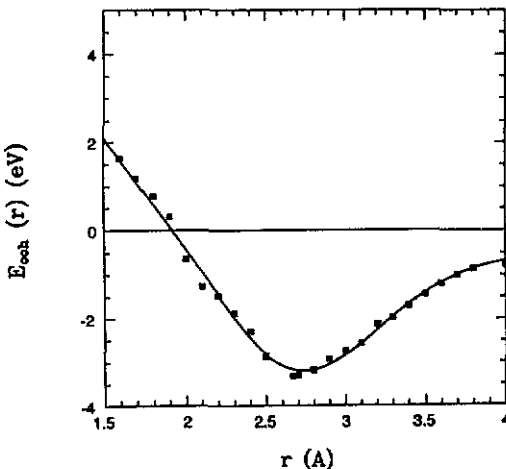


Figure 1. The cohesive energy of copper versus the lattice constant. The full squares are the calculated values, and the full curve is the best-fit function.

In figure 2 we show our main results. The full curve shows the pair potential calculated from six terms in the series (7), while the dotted curve shows the estimate from the first term, i.e. $\Re E(r)$ alone. The contribution from the remaining terms is also shown in the figure (dashed curve). Most of these contributions occur at small

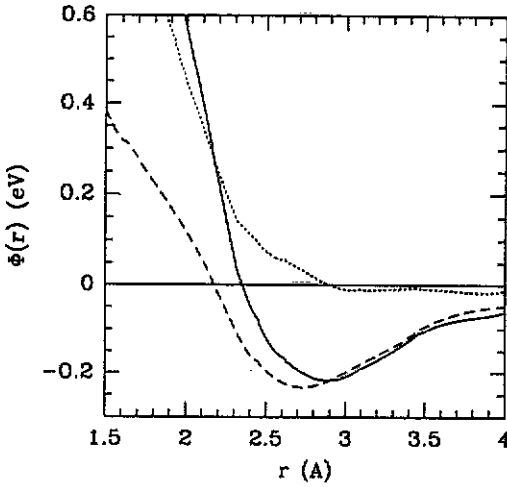


Figure 2. The pair potential as a function of the distance between atoms. The dashed curve represents the term $8E(r)$. The full curve is the converged curve after taking into account six terms in the series (7). The dotted curve shows the correction to the first term (dashed curve) coming from the rest of the lattice.

values of r . This is a reflection of the fact that $E(r)$ rapidly converges to zero for $r/r_e \approx 3$. Inclusion of more terms in the series hardly changes the pair potentials and those curves will be indistinguishable from the full curve to this degree of accuracy.

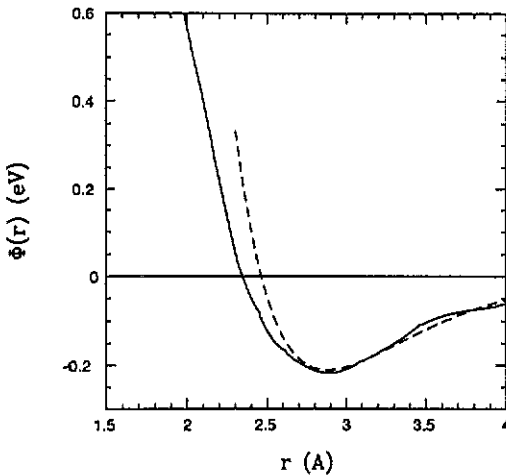


Figure 3. The pair potential as a function of r . The full curve shows our calculation and the dashed curve the Morse-type fitted potential reported by Johnson (1988).

Figure 3 shows the pair potential from our calculation (full curve) along with the results of Johnson (1989) (dotted curve) obtained from the embedded-atom method. It can be noted that while the potential has a form similar to the cohesive energy it is about an order of magnitude smaller. This should have been clear from the weight

of $(1/6)$ in expression (11) for N . Furthermore, our pair potential has a minimum at 2.89 \AA . This shift of the minimum of the pair potential as compared with that of the cohesive energy is very similar to the estimate of Carlsson *et al* (1980). Also, as with their case, the range of the pair potential is effectively about twice the equilibrium value of r_e , beyond which it falls exponentially to zero. Johnson (1989), obtained a Morse-type potential using the embedded-atom method and from fitting the cohesive energy, bulk modulus and vacancy formation energies. Though this curve is similar to our results, the minima of the two potentials are shifted. The agreement for the more interesting region of $r > r_e$ is surprisingly very good whereas there are discrepancies in the $r < r_e$ regime. We do not expect the pair potential of Johnson (1989) to be as good in this regime as for $r > r_e$. Also our calculations of the cohesive energy may require refinement as can be seen from figure 1 where the fit to the actual points is very good for $r > r_e$ but not so good for $r < r_e$.

In conclusion we have applied the method of Möbius transformation to the problem of inversion of the cohesive energy to obtain an *ab initio* pair potential for FCC metals and have tested it for copper. This method is fast, accurate and easily implemented on even a small personal computer. Once the difficult task of accurately evaluating the cohesive energy from first principles is over, the methodology described is ideally suited to obtain the pair potential and from it various measurable physical quantities.

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