Indian J. Phys. **75A** (1), 21-23 (2001)

IJP A
an international journal

On the extraction of effective pair interaction of simple metals from third order pseudopotential energy

D Sen*, A Sarkar** and S Haldar†

Condensed Matter Physics Research Centre, Department of Physics,
Jadavpur University, Calcutta-700 032, India

Abstract : Complete expression of the additional pair interaction due to the third-order energy term in the electron-ion interaction is lacking in the literature We present here the formulation of the pair interaction from third-order energy term An estimate of the additional terms with localised *ab initio* pseudopotential is made and found to produce good agreement with improved recent calculations

Keywords . Pseudopotential theory of metals, effective interaction, perturbation theory

PACS Nos. . 34 20.Cf, 71.15.Hx, 63 10+a

1. Introduction

The pseudopotential approach is most powerful in its application to the theory of metals for its amenability to a perturbative calculation. There are several indications [1-4] that third- and fourth-order terms play an important role in the lattice mechanical properties of metals. The total energy of a metal, according to pseudopotential theory, may be expressed in terms of density dependent interionic interactions in addition to the volume dependent energy. A real space description of systems in terms of effective interactions is very useful in material physics for several reasons. Besides providing improved interpretability and direct understanding of structural stability and relaxation phenomena in simpler terms, it offers viable computational schemes for simulation of complex material science problems.

Interionic interaction of simple metals, within the framework of linear screening theory due to the third-order perturbation term in the electron-ion pseudopotential, was developed earlier by Hasegawa [5]. The importance of the additional pair potential term in determining the structural and thermodynamic properties of liquid metals has also been discussed. However, Hasegawa has considered the two symmetric terms only and omitted a third term of comparable magnitude. The derivation of the expression for this term is some what complicated like that of the three – ion interaction, but after simplification it turns out to be exactly equal to the symmetric terms. The purpose of the present paper is to discuss the formulation [6] of the full expression of the additional pair interaction $V^3(r)$ due to the third order term in electron-ion pseudopotential.

* Corresponding Author
Barasat Govt. College, Barasat-743 201, West Bengal, India.
** B. K. Girls' College, Howrah-711 101, West Bengal, India
† Asansol Engineering College, Asansol-4, West Bengal, India.
E-mail : sandeep@juphys.ernet.in

2. Formulation

Third-order energy and interionic potentials within local approximation :

The third-order band structure energy is given by [7]

$$E_3 = \Omega \sum_{q_1 q_2}{}' S_{q_1} S_{q_2} S_{-q_1 - q_2} \omega_{q_1} \omega_{q_2} \omega_{|q_1+q_2|} g(q_1, q_2, |q_1+q_2|), \tag{1}$$

where $q_i = |q_i|$, the primed sums exclude null q_i and Ω is the ionic volume. The structure factor S_q is defined as

$$S_q = \frac{1}{N} \sum_k \exp(-iq.r_k),$$

N being the total number of ions. The screened pseudopotential form factor ω_q are plane wave matrix elements of bare ion-electron pseudopotential divided by the dielectric function, g is

the symmetric function of the three modulii q_1, q_2 and q_3 [7]. Writing formally $\varepsilon_3(q_1, q_2, q_3) = \Omega^3 \omega_{q_1} \omega_{q_2} \omega_{q_3} g(q_1, q_2, q_3)$, E_3 may be written as

$$E_3 = \Omega^{-2} N^{-3} \sum_{q_1 q_2}{}' \sum_{klm}{}' e^{-iq_1 r_k} e^{-iq_2 r_l} e^{i(q_1+q_2) r_m} \varepsilon_3$$

$$= \Omega^{-2} N^{-3} \sum_{q_1 q_2}{}' \left[\sum_{k=l=m} \varepsilon_3 + \sum_{k=m\neq l} \varepsilon_3 e^{-iq_2 (r_l - r_m)} \right.$$

$$+ \sum_{k\neq l=m} \varepsilon_3 e^{-iq_1 (r_k - r_m)} + \sum_{k=l\neq m} \varepsilon_3 e^{-i(q_1+q_2)(r_l - r_m)}$$

$$\left. + \sum_{k\neq l\neq m} \varepsilon_3 e^{-iq_1 (r_k - r_m)} e^{-iq_2 (r_l - r_m)} \right]. \qquad (2)$$

The first term represent one-body potential or the volume dependent part of the energy and is out of our present consideration. From symmetry the second and third terms give identical contributions to the two body (central) interaction and together represent $\phi_2^3(r)$ of Hasegawa's eq. (3). The 4th term also represents (central) pair interaction of comparable magnitude and was missed out in Hasegawa's work. The 5th term gives the three-body interaction of E_3.

2a. Simplification of two body part from the 2nd and 3rd terms:

The two identical terms may be expressed as

$$E_3^2 = \Omega^{-2} N^{-3} \sum_{q_1 q_2}{}' \sum_{kl}{}' \varepsilon_3 e^{-iq_1 r_{kl}}$$

$$= \frac{1}{2N} \left[\frac{2}{(N\Omega)^2} \sum_{kl}{}' \sum_{q_1 q_2}{}' \varepsilon_3 e^{-iq_1 r_{kl}} \right]$$

$$= \frac{1}{2N} \sum_{kl}{}' \left[\frac{2}{(N\Omega)^2} \sum_{q_1 q_2}{}' \varepsilon_3 e^{-iq_1 r_{kl}} \right].$$

We include null q in the summation and write

$$v^3(r) = \frac{2}{(N\Omega)^2} \sum_{q_1 q_2} \varepsilon_3 e^{-iq_1 \cdot r},$$

where $v^3(r)$ is a part of two-body interaction from 3rd order perturbation. Replacing Σ_q by $\frac{N\Omega}{(2\pi)^3} \int dq$ we get

$$v^3(r) = \frac{2}{(N\Omega)^2} \frac{(N\Omega)^2}{(2\pi)^6} \iint \varepsilon_3(q_1, q_2, q_3)\, e^{-iq_1 \cdot r}\, dq_1\, dq_2$$

$$= \frac{1}{8\pi^4} \iint\!\!\iint \varepsilon_3(q_1, q_2, q_3) e^{-iq_1 r} q_1^2 q_2^2\, dq_1 dq_2 d\cos\theta_1 d\cos\theta_2 .$$

First we consider r as the polar axis and $\theta_1 = \theta_{q_1 r}$. The above integral may be written as

$$8\pi^4 \int q^2\, dq_1 \int q_2^2\, dq_2 \int d\cos\theta_2\, \varepsilon_3(q_1, q_2, q_3)$$

$$\int e^{-iq_1 r \cos\theta_{q_1 r}} d\cos\theta_{q_1 r}$$

$$4\pi \int q^2\, dq_1 \int q_2^2\, dq_2 \int d\cos\theta_2\, \varepsilon_3(q_1, q_2, q_3) \frac{\sin(q_1 r)}{q_1 r}$$

The θ_2 integration may be performed using q_1 as the polar axis *i.e.* putting $\theta_2 \equiv \theta_{q_1 q_2} \equiv \theta$ and expressing ε_3 formally as $\varepsilon_3(q_1, q_2, \theta)$ we finally write

$$v^3(r) = \frac{1}{4\pi^4} \iiint \varepsilon_3(q_1, q_2, \theta) \frac{\sin(q_1 r)}{q_1 r} q_1^2\, dq_1\, q_2^2\, dq_2 d\cos\theta.$$

2b. Contribution to $V^3(r)$ from the 4th term:

The fourth term similarly gives rise to a pair interaction of the form

$$v'^3(r) = \frac{2}{(2\pi)^6} \iint \varepsilon_3(q_1, q_2, \theta_{q_1 q_2})\, e^{-i(q_1+q_2) r}\, dq_1 dq_2 . \qquad (3)$$

First we consider the q_2 integration by taking q_1 as the polar axis. We note

$$q_2 . r = q_2 r \cos\theta_{q_2 r}$$

$$= q_2 r \left(\cos\theta_{q_1 q_2} \cos\theta_{q_1 r} + \sin\theta_{q_1 q_2} \sin\theta_{q_1 r} \cos\phi \right), \qquad (4)$$

where ϕ is the angle between (q_1, q_2) and (q_1, r) planes. Using eq. (4) the integration over ϕ can be expressed in terms of the zeroth-order Bessel function of the first kind :

$$\int_0^{2\pi} d\phi \exp(-iQ\cos\phi) = 2\pi J_0(Q),$$

where $Q = q_2 r \sin\theta_{q_1 q_2} \sin\theta_{q_1 r}$. We then have

$$v'^3(r) = \frac{2}{(2\pi)^5} \int dq_1 \exp(-iq_1 . r) \int q_2^2\, dq_2 \int \varepsilon_3(q_1, q_2, \theta_{q_1 q_2})$$

$$J_0(Q) \exp(-iq_2 r \cos\theta_{q_1 q_2} \cos\theta_{q_1 r}) d\cos\theta_{q_1 q_2} .$$

For q_1 integration we now take r as the polar axis. Proceeding in a similar manner we get

$$v'^3(r) = \frac{2}{(2\pi)^4} \int q_1^2 dq_1 \int d\cos\theta_{q_1 r} \exp(-iq_1 r \cos\theta_{q_1 r})$$

$$\int q_2^2 dq_2 \int \varepsilon_3(q_1, q_2, \theta_{q_1 q_2})\, J_0(Q)$$

$$\exp(-iq_2 r \cos\theta_{q_1 q_2} \cos\theta_{q_1 r}) d\cos\theta_{q_1 q_2} .$$

Changing a variable $x = \cos\theta_{q_1 r}$, we get

$$v'^3(r) = \frac{1}{4\pi^4}\int q_1^2 dq_1 \int q_2^2 dq_2 \int \varepsilon_3(q_1, q_2, \theta_{q_1 q_2}) d\cos\theta_{q_1 q_2}$$

$$\int_0^1 dx\, J_0(Q)\cos\left[(q_1 r + q_2 r\cos\theta_{q_1 q_2})\lambda\right].$$

The last integral can be evaluated analytically. Putting $Q = q_2 r \sin\theta_{q_1 q_2}(1-x^2)^{1/2} = \alpha(1-x^2)^{1/2}$ and $\beta = (q_1 + q_2\cos\theta_{q_1 q_2})\, r$, the integral is [8]

$$\int_0^1 J_0\left(\alpha(1-x^2)^{1/2}\right)\cos\beta x dx = \frac{\sin(\alpha^2+\beta^2)^{1/2}}{(\alpha^2+\beta^2)^{1/2}}$$

Finally,

$$v'^3(r) = \frac{1}{4\pi^4}\iiint \varepsilon_3(q_1, q_2, \theta) q_1^2\, q_2^2 \frac{\sin(\alpha^2+\beta^2)^{1/2}}{(\alpha^2+\beta^2)^{1/2}}$$

$$dq_1\, dq_2\, d\cos\theta$$

$$4\pi^4 \iiint \varepsilon_3(q_1, q_2, \theta) q_1^2\, q_2^2 \frac{\sin(|q_1+q_2|r)}{|q_1+q_2|r} d\cos\theta\, dq_1\, dq_2$$

The integral is actually identical to that for $V^3(r)$ and the total third-order contribution $V^3(r)$ to the pair interaction is, therefore, given by

$$V^3(r) = 2v^3(r) + v'^3(r)$$

$$= \frac{3}{4\pi^4}\iiint \varepsilon_3(q_1, q_2, \theta) q_1^2\, q_2^2 \frac{\sin(q_1 r)}{q_1 r} d\cos\theta\, dq_1\, dq_2$$

3. Discussion

The third order contribution depends considerably on the form factors at large q. The estimate of the additional terms with a local or an "on-Fermi-Sphere" approximated pseudopotential form factor, having spurious large q oscillations, is therefore always suspect. Calculation with *ab initio* pseudopotential form factor is expected to provide a reliable estimate of the additional term. However, the perturbation series with the *ab initio* pseudopotential form factor is an oscillating one and the energy upto third-order term is not quite reliable for the determination of the equilibrium lattice parameters (s) [3]. Application of convergence acceleration method to the perturbation series sequence is found to produce excellent stable result for the total energy. Also, the average values of phonon frequencies upto third-order reproduce [3] the observed phonon dispersion curves almost exactly. Similarly in this case, the resulting average pair interaction upto third-order compares well [9] with recently developed calculation [10] based on large set of experimental and *ab initio* data

Acknowledgment

One of the authors (SH) acknowledges financial support of UGC (University Grants Commission), India.

References

[1] C M Bertoni, O Bisi, C Calandra and F Nizzoli *J Phys* **F5** 419 (1975)

[2] J Hammerberg and N W Ashcroft *Phys Rev* **B9** 409 (1974)

[3] D Sen *Phys Rev* **B 42** 1217 (1990)

[4] B Dutta, D Sen and D Roy *Physica* **B210** 73 (1995)

[5] M Hasegawa *J Phys* **F6** 649 (1976)

[6] D Sen CMPRC Internal Research Report 1996-97 (unpublished)

[7] P Lloyd and C Sholl *J Phys* **C1** 1620 (1968)

[8] I S Gradshteyn and I M Ryzhik *Table of Integrals, Series and Products* (New York : Academic) p 737 (1965)

[9] S Haldar, A Sarkar and D Sen *CMDAYS-99* (CMPRC, Jadavpur University, Calcutta) *Indian J Phys* **75A** 25 (2001)

[10] Y Mishin, D Farkas, M J Mehl and D A Papaconstantopoulos *Phys Rev* **B59** 3393 (1999)