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Density-dependent potentials for simple metals

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Abstract. We have calculated the total energy for a simple metal within pseudopotential theory to second order in the pseudopotential. Our work is based on a first-principles non-local pseudopotential. The results presented here contain an extra term accounting for the density dependence of the higher-order terms in the total energy. This term is required to equilibrate the system at the observed density and should be included in any low-order expansion of the total energy. A closed-form expression for the energy–wavenumber characteristic is given, from which the pair potential can readily be obtained by a Fourier transform. Also included is a simple and accurate expression for the local field, which gives the electron gas screening.

1. Introduction

An important characteristic of a metal is that its properties are generally dominated by the conduction electrons. For example, the Coulomb repulsion between the ions is heavily screened by the conduction electrons, giving rise to relatively weak interatomic potentials. This characteristic is especially evident in the simple metals, i.e. metals whose conduction electrons are nearly free-electron-like. In such metals, the cohesive energy is derived almost entirely from the conduction electrons, the contribution of the interatomic interactions being typically one-tenth of the total cohesive energy.

Owing to the presence of the conduction electrons, the approximation of density-independent pair potentials frequently used in molecular dynamics and Monte Carlo simulations breaks down. The extent to which this approximation is invalid is shown by the breakdown of the Cauchy relation, which states that, for a crystal in equilibrium under central forces alone, $C_{12}-C_{44}$ is zero, where C_{ij} refers to the elastic constants. Finnis (1974) has shown that, for a simple metal, $C_{12}-C_{44}$ is determined by the density dependence of the total energy by deriving an explicit expression for this quantity in terms of the density derivatives of contributions to the total energy. The importance of the density dependence of the total energy in determining the structure of a metal has been discussed in the review by Heine and Weaire (1970).

Because of the weak effective ion–electron interactions in the simple metals, the total energy can be treated by perturbation theory, with the homogeneous electron gas

as the unperturbed system. By going to second order in the strength of the ion–electron interaction, the total energy takes the form (Finnish 1974)

$$U_{\text{tot}} = U_0(\rho) + (0.5/N) \sum'_{m,m'} \varphi(|\mathbf{R}_m - \mathbf{R}_{m'}|, \rho) \quad (1.1)$$

where ρ is the conduction electron density, N is the number of ions, \mathbf{R}_m is the position of the m th ion and the prime on the summation excludes $m = m'$. The ‘volume term’ U_0 and the effective pair potential φ are strongly dependent on ρ . In this paper we discuss the volume and structural terms for a theory of interatomic interactions based on a non-local pseudopotential. We have generalized the paper by Finnis (1974) for the volume term to cover non-local pseudopotentials and have calculated the equilibrium volume, Ω_0 , with linearly screened pseudopotentials whose parameters are obtained from first-principles theory.

The motivation for this work is the influence of the density dependence of U_0 and φ on many phenomena in metals, such as structural phase transitions and grain boundary structures. The density variation may in the case of defects take place on an atomic scale. There are now simulation methods such as the variable cell molecular dynamics (Parrinello and Rahman 1980) where the density dependence can be allowed for. In this paper and the following paper (Walker and Taylor 1990), hereafter referred to as paper II, we provide expressions for U_0 and φ in forms that can easily be used in such schemes.

An unexpected result is that our predicted Ω_0 is found to be considerably less than the observed value for simple metals. The origin of this discrepancy is discussed in section 4.1. There we show that an extra term U_{HO} must be included in the total energy in order to represent the effect of the density dependence of the terms beyond second order in perturbation theory. We provide a simple expression for U_{HO} where we use a single adjustable parameter, μ , to achieve the observed Ω_0 . Here we give results for U_{tot} including this extra term for Li, Na, Al and K.

We have chosen non-local pseudopotential theory, despite the fact that the algebra is more complicated than for local pseudopotentials, for three reasons. The first reason is that it is often useful to compare how a given pseudopotential explains a variety of phenomena and most properties of metals cannot be well predicted by local pseudopotentials. One example is the cohesive energy, which Chelikowsky (1981) has demonstrated is strongly sensitive to non-locality. Another case is electron transport (Taylor 1982). For instance, the reduced thermopower is necessarily 3 or less for a local pseudopotential, whereas the experimental value for K (for which a local pseudopotential is normally considered adequate) is about 4 at high temperatures (Cook and Laubitz 1976).

Secondly, for model local pseudopotentials, the parameters have to be fitted to some experimental property. In many cases, because the local pseudopotential does not adequately represent the electron–ion interaction, a pseudopotential fitted to one property needs readjustment for another. Manninen *et al* (1981) have overcome this disadvantage by developing a scheme for *ab initio* calculations of interatomic potentials of simple metals with a local pseudopotential. We will discuss their scheme in section 4.2.

Thirdly, a prime motivation for our calculation was the difficulty Walker *et al* (1986) had in reproducing the structural phase diagram of Li. It is likely that the phase transitions are driven by the difference in the free energy between the two structures, which is controlled by the effective ion–ion interaction. The effective potential used by Walker *et al* (1986) was based on a local pseudopotential. The fact that it gives phonon dispersion curves that do not agree well with experiment (A B Walker, unpublished) suggests strongly that it may not accurately predict the dynamic behaviour of the system. In

the following paper, paper II (Walker and Taylor 1990), we derive a simple analytic representation for U_0 and the interionic potential of Dagens, Rasolt and Taylor (DRT) (Rasolt and Taylor 1975, Dagens *et al* 1975). The phonons from the DRT potential give excellent agreement with experiment, so we anticipate that the potentials described in paper II will overcome the problems experienced by Walker *et al* (1986) and Finnish and Sachdev (1976).

The layout of our paper is as follows. In section 2 we derive an expression for the total energy to second order in the pseudopotential. Section 3 presents accurate analytic representations for the 'local' component $F_L(q)$ of the energy-wavenumber characteristic $F(q)$, from which the effective pair potential is obtained. Our results for U_{tot} for Li, Na, Al and K are in section 4.1. Section 4.2 contains $F_L(q)$, the 'non-local' component $F_{\text{NL}}(q)$, $F(q)$ and the pair potential calculated for Li, and the method of Manninen *et al* (1981) is discussed. Our conclusions are in section 5. Appendix 1 contains the expansions for $F(q)$, and finally, in appendix 2 we give expressions for the local field based on the analysis by Vosko *et al* (1980).

2. The total energy

In this section we derive expressions for the total energy for a system of ions and conduction electrons to second order in the pseudopotential governing electron-ion interactions. Our theory uses the formulation of Rasolt and Taylor (1975), hereafter referred to as RT, to find an expression for the volume term U_0 , which is given here for the first time for non-local pseudopotentials. We show that our expression for U_0 is identical to that derived by Finnis (1974) for a local pseudopotential except for an additional term, U_{NL} , and the way in which the terms involving the pseudopotential are calculated.

The total energy per ion of N ions of charge Z in units of the electronic charge e in a volume Ω is given by

$$\begin{aligned}
 U_{\text{tot}} = & (2/N) \sum_k \theta(k_F - k) E_k - (0.5/N) \int n(\mathbf{r}) n(\mathbf{r}') v_c(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r} d\mathbf{r}' + (1/N) E_{\text{XC}}[n] \\
 & - (1/N) \int v_{\text{XC}}(n) n(\mathbf{r}) d\mathbf{r} + (0.5Z^2/N) \sum' \int d\mathbf{r} d\mathbf{r}' v_c(|\mathbf{r} - \mathbf{r}'|) [\delta(\mathbf{r} - \mathbf{R}_m) \\
 & - 1/\Omega] [\delta(\mathbf{r} - \mathbf{R}_{m'}) - 1/\Omega]
 \end{aligned} \tag{2.1}$$

where $\theta(x)$ is the unit step function and k_F is the Fermi wavevector. The E_k are the energy eigenvalues for the electron gas of density $n(\mathbf{r})$ with a uniform positive background of density $n_0 = NZ/\Omega$ and $n(\mathbf{r}) = n(\mathbf{r}) - n_0$. The term E_{XC} is the exchange-correlation functional, $v_{\text{XC}}(n) = (1/\Omega) \delta E_{\text{XC}}[n] / \delta n$ is the exchange-correlation potential, and the Coulomb potential $v_c(r) = e^2 / (4\pi\epsilon_0 r)$ (e is the electron charge and ϵ_0 is the vacuum permittivity). The third and fourth terms are subtracted to avoid double counting electron-electron interactions. Ion-ion Coulomb interactions are represented in the final term, taking into account the uniform positive background.

From the theory presented in RT, E_k is the eigenvalue for the total energy comprising the kinetic energy operator T and the potential V_T representing electron–electron and electron–ion interactions; thus

$$(T + V_T)|\varphi_k\rangle = E_k|\varphi_k\rangle \quad (2.2)$$

where $|\varphi_k\rangle$ is the eigenstate of momentum \mathbf{k} ,

$$\langle \mathbf{r} | T | \mathbf{r}' \rangle = -[\hbar^2 \nabla^2 / (2m)] \Omega \delta(\mathbf{r} - \mathbf{r}') \quad (2.3)$$

$$\langle \mathbf{r} | V_T | \mathbf{r}' \rangle = \sum_m v_p(\mathbf{r} - \mathbf{R}_m, \mathbf{r}' - \mathbf{R}_m) \left(\int n(\mathbf{r}'') v_c(|\mathbf{r} - \mathbf{r}''|) d\mathbf{r}'' + v_{XC}(n) \right) \Omega \delta(\mathbf{r} - \mathbf{r}'). \quad (2.4)$$

Here v_p is the non-local pseudopotential operator and m is the electron mass.

To second order in V_T ,

$$E_k = \varepsilon_k + \langle \mathbf{k} | V_T | \mathbf{k} \rangle + \sum_q' |\langle \mathbf{k} | V_T | \mathbf{k} + \mathbf{q} \rangle|^2 / (\varepsilon_k - \varepsilon_{\mathbf{k}+\mathbf{q}}) \quad (2.5)$$

where $\varepsilon_k = \hbar^2 k^2 / (2m)$ and the prime on the summation implies exclusion of $\mathbf{q} = 0$. Therefore

$$E_k = \varepsilon_k + \lim_{q \rightarrow 0} \langle \mathbf{k} | S(\mathbf{q}) v_p + Z v_c(\mathbf{q}) | \mathbf{k} + \mathbf{q} \rangle + \sum_q' |\langle \mathbf{k} | S(\mathbf{q}) v_p | \mathbf{k} + \mathbf{q} \rangle + n(\mathbf{q}) \Omega v_c(\mathbf{q}) + 2n(\mathbf{q}) K_{XC}(\mathbf{q})|^2 / (\varepsilon_k - \varepsilon_{\mathbf{k}+\mathbf{q}}). \quad (2.6)$$

Here ε_F is the Fermi energy, the exchange correlation kernel $K_{XC}(\mathbf{r}, \mathbf{r}') = (1/\Omega) \delta^2 E_{XC}[n] / \delta n(\mathbf{r}) \delta n(\mathbf{r}')$ and $S(\mathbf{q}) = \sum \exp(-i\mathbf{q} \cdot \mathbf{R}_m)$, where the sum is over lattice sites \mathbf{R}_m . The second term in equation (2.6) contains a contribution $Z v_c(\mathbf{q})$, which compensates for the fact that the uniform charge background is already included in the zeroth-order term. We use the following formulae to simplify equation (2.1):

$$1/\chi(\mathbf{q}) = 1/\Pi_0(\mathbf{q}) + \Omega v_c(\mathbf{q}) + 2K_{XC}(\mathbf{q}) \quad (2.7)$$

(Geldart *et al* 1972) where χ is the susceptibility, the free-electron polarizability

$$\Pi_0(\mathbf{q}) = -(4/\Omega) \sum_k \theta(k_F - k) / (\varepsilon_k - \varepsilon_{\mathbf{k}+\mathbf{q}}) \quad (2.8)$$

and

$$E_{XC}[n] = E_{XC}[n_0] + (0.5/\Omega) \int K_{XC}(\mathbf{r}, \mathbf{r}') n(\mathbf{r}) n(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (2.9)$$

Also, from RT,

$$n(\mathbf{q}) = -\bar{v}_p \chi(\mathbf{q}) S(\mathbf{q}) \quad (2.10)$$

where

$$\bar{v}_p = -(4/\Pi_0 \Omega) \sum_k \theta(k_F - k) \langle \mathbf{k} + \mathbf{q} | v_p | \mathbf{k} \rangle / (\varepsilon_k - \varepsilon_{\mathbf{k}+\mathbf{q}}). \quad (2.11)$$

\bar{v}_p is a weighted average of the electron-ion matrix elements (Taylor and Macdonald 1980). Similarly we define

$$\bar{v}_p^2 = -(4/\Pi_0\Omega) \sum_k |\langle \mathbf{k} + \mathbf{q} | v_p | \mathbf{k} \rangle|^2 / (\epsilon_k - \epsilon_{k+\mathbf{q}}). \quad (2.12)$$

From equations (2.1) to (2.12), we obtain

$$\begin{aligned} U_{\text{tot}} = & 0.6Z\epsilon_F + (1/N)E_{\text{XC}}[n_0] + \lim_{q \rightarrow 0} \left(2 \sum_k \theta(k_F - k) \langle \mathbf{k} | [S(\mathbf{q})/N] v_p | \mathbf{k} \rangle \right. \\ & \left. + 0.5Z^2[v_c(\mathbf{q}) + F(\mathbf{q})v_c(\mathbf{q})] \right) + 0.5(Z^2/N) \sum'_{m,m'} v_c(|\mathbf{R}_m - \mathbf{R}_{m'}|) \\ & - 0.5(Z^2/N) \sum_q |S(\mathbf{q})|^2 F(\mathbf{q})v_c(\mathbf{q}) \end{aligned} \quad (2.13)$$

where the energy-wavenumber characteristic

$$F(\mathbf{q}) = F_L(\mathbf{q}) + F_{\text{NL}}(\mathbf{q}) \quad (2.14)$$

for

$$F_L(\mathbf{q}) = (\bar{v}_p)^2 \chi \Omega / (Z^2 v_c) \quad (2.15)$$

and

$$F_{\text{NL}}(\mathbf{q}) = [\bar{v}_p^2 - (\bar{v}_p)^2] \Omega \Pi_0 / (Z^2 v_c) \quad (2.16)$$

(Taylor and MacDonald 1980). By adding and subtracting $\lim_{q \rightarrow 0} \bar{v}_p(\mathbf{q})$ from the third term in equation (2.13), our final result for U_{tot} is then

$$U_{\text{tot}}(\rho) = U_0(\rho) + U_{\text{II}}(\rho) \quad (2.17)$$

where

$$U_0(\rho) = U_L + U_{\text{NL}} \quad (2.18)$$

$$U_L = U_{\text{EG}} - 0.5Z^2\Omega^2 \partial^2 U_{\text{EG}} / \partial \Omega^2 + U_{\text{BS}} \quad (2.19)$$

$$E_{\text{EG}} = 0.6Z\epsilon_F + E_{\text{XC}}[n_0]/N \quad (2.20)$$

$$U_{\text{BS}} = -0.5Z^2 \sum_q F(\mathbf{q})v_c(\mathbf{q}) \quad (2.21)$$

$$U_{\text{NL}} = \lim_{q \rightarrow 0} (2/N) \sum_k \theta(k_F - k) [\langle \mathbf{k} + \mathbf{q} | v_p | \mathbf{k} \rangle - \bar{v}_p(\mathbf{q})] \quad (2.22)$$

$$U_{\text{II}} = (0.5/N) \sum'_{m,m'} \varphi(|\mathbf{R}_m - \mathbf{R}_{m'}|, \rho) \quad (2.23)$$

$$\varphi(r, \rho) = Z^2 v_c(r) - Z^2 \sum_q F(\mathbf{q}, \rho) v_c(\mathbf{q}) e^{iq \cdot r}. \quad (2.24)$$

Note that U_{NL} is zero for a local pseudopotential.

3. The energy-wavenumber characteristic

In this section we derive an accurate analytic representation of $F_L(\mathbf{q})$ from its behaviour at small and large q . Since $F_L(\mathbf{q})$ dominates the effective pair potential, as demonstrated

for Li in section 4.2, these expressions will provide a means of generating an accurate pair potential via equation (2.24) as an alternative to the form for φ derived in paper II.

Whilst the theory presented in section 2 is valid for any energy-independent pseudopotential, we have used a Heine–Abarenkov pseudopotential for the analytical results presented in this paper and paper II, viz.

$$v_p = -Zv_c(r) + \theta(R_M - r)[v_c(r) + A_2 + (A_0 - A_2)P_0 + (A_1 - A_2)P_1]. \quad (3.1)$$

Here P_l is the angular momentum projection operator for angular momentum l . Note that we have used the Heine–Abarenkov form of pseudopotential in both this paper and paper II to present analytical results (section 3) and numerical results (section 4) because these results are simpler than they would be for other model pseudopotentials. Furthermore, the Li pseudopotential of Dagens *et al* (1975)—for which further results are presented in paper II—adopts the Heine–Abarenkov form, obtaining the values of the parameters A_i ($i = 0, 1, 2$) and R_M from a first-principles calculation described in section 4.1. However, our fitting procedures will work for any form of linearly screened pseudopotential and do not rely on a Heine–Abarenkov pseudopotential.

We have found a simple analytic expression for $F_L(q)$ by writing it in terms of the non-local integrals \bar{L}_0 and \bar{L}_1 defined in appendix 1. The expressions were obtained by interpolation between expansions of the integrals at low q and high q in powers of q'^2 and $1/q'^2$, respectively, where $q' = q/k_F$. Since these expansions are also used to find a pair potential derived from $F(q)$, as discussed in paper II, we have given them in appendix 1. Inserting (3.1) into (2.11) and using the symmetrization and transformation-of-variables technique described in section III of RT, we find that

$$\bar{v}_p/[Zv_c(q)] = M_L(q) + q'^2(\alpha_0\bar{L}_0 + 3\alpha_1\bar{L}_1) \quad (3.2)$$

where

$$M_L(q) = A'_2R' \sin(q'R')/(q'R') - (A'_2R' + 1) \cos(q'R') \quad (3.3)$$

$$A'_i = A_i/[Ze^2k_F/(4\pi\epsilon_0)] \quad i = 0, 1, 2 \quad R' = R_Mk_F \quad (3.4)$$

$$\alpha_i = A'_i - A'_2. \quad (3.5)$$

Using (2.12) a similar expression can be derived for \bar{v}_p^2 . From this expression and from equations (3.2)–(3.5), (2.15) and (2.16),

$$F_L(q) = Z^2\Omega v_c(q)\chi(q)[M_L(q) + q'^2(\alpha_0\bar{L}_0 + 3\alpha_1\bar{L}_1)]^2 \quad (3.6)$$

$$F_{NL}(q) = Z^2\Omega v_c(q)\Pi_0(q)q'^4\{\alpha_0^2[\bar{L}_{00} - (\bar{L}_0)^2] + 6\alpha_0\alpha_1(\bar{L}_{01} - \bar{L}_0\bar{L}_1) + 9\alpha_1^2[\bar{L}_{11} - (\bar{L}_1)^2]\} \quad (3.7)$$

where the non-local integrals \bar{L}_0 , \bar{L}_1 , \bar{L}_{00} , \bar{L}_{01} and \bar{L}_{11} are given by equations (A1.1)–(A1.8) and following sentence in appendix 1. These integrals have to be evaluated numerically, which can be very time-consuming if one constantly has to re-evaluate the pair potential at different densities. By examining the small- and large- q expansions of the most significant of the integrals, \bar{L}_0 and \bar{L}_1 , we have obtained the following analytical representations of them:

$$\bar{L}_0 = -s'\{3j_1(q'R')/(q'R') + [j_2(q'R') + j_4(q'R')g_0(q')]/4\} \quad (3.8)$$

$$\bar{L}_1 = -[s'/4 + R'^2j_1(q'R')j_0(q'R')][3j_1(q'R')/(q'R') + 2X/3] + s'X/12 \quad (3.9)$$

where

$$X = \{j_2(q'R') + [q'R'j_3(q'R')/2 + j_4(q'R')g_0(q')]\}g_0(q') \quad (3.10)$$

$$s' = \sin(2R') - 2R' \quad (3.11)$$

$$g_0(q') = [2 - f_0(q')]f_0(q') \quad (3.12)$$

and $f_0(q')$ is the Lindhard function, i.e.

$$f_0(x) = \frac{1}{2} + (1 - x^2)[\log|(1+x)/(1-x)|]/(4x). \quad (3.13)$$

The functions $j_i(q)$ are the spherical Bessel functions of order i . Equations (3.8) and (3.9) are exact in the small- and large- q limits and accurate to better than 1.5% of the $q = 0$ value, except for a small range of q values near $q = 2k_F$ in the case of \bar{L}_0 , where the errors are still less than 3%. The zeros in both functions are correctly reproduced by equations (3.8) and (3.9).

4. Results

4.1. Total energy

Table 1 lists the contributions to the total energy as a function of density ρ in units of the equilibrium density ρ_0 for Li, Na, Al and K. In the table U_L represents the contribution to the total energy that would be present for a local pseudopotential, U_{NL} is the term that is purely due to non-local effects, U_0 is the volume term, U_{II} is the structure term, U_{tot} is the total energy from pseudopotential theory (equation (2.17)), U_{HO} is the correction term due to the density dependence of terms beyond second order in the pseudopotential (and is discussed below) and \bar{U}_{tot} is the total energy including U_{HO} . Thus

$$\bar{U}_{tot} = \bar{U}_0 + U_{II} \quad (4.1)$$

where \bar{U}_0 is the corrected volume term, i.e.

$$\bar{U}_0 = U_0 + U_{HO}. \quad (4.2)$$

All the numbers in the tables and the figures were found using the first-principles pseudopotentials and lattice constants specified in Dagens *et al* (1975) except for Na where the corrected pseudopotential parameters of Cohen *et al* (1976) were used and for Li where the lattice parameter of 4.382 Å in the FCC phase (equivalent to 3.478 Å for the BCC lattice at low temperatures (Beg and Nielsen 1976)) was used.

U_0 was evaluated from equation (2.18) using the following procedure. The electron-gas terms in U_L (equation (2.19)) were calculated from the formalism presented in appendix 2 where the expressions of Vosko *et al* (1980) were used for the local field although the approximate expression given in equation (A2.4) would give almost precisely the same result. The band-structure term U_{BS} was found from the expression for $F(q)$ given in section 3, equations (3.2)–(3.7), using the definitions of the non-local integrals given in appendix 1, equations (A1.1)–(A1.8). U_{NL} (equation (2.22)) was calculated from \bar{v}_p , which is given in terms of the non-local integrals in equation (3.2). Here also the non-local integrals were evaluated from their definitions in (A1.1)–(A1.8). To find U_{II} (equation (2.23)), we used equation (2.24) for the pair potential and evaluated $F(q)$ using the formalism described above.

Table 1 shows clearly that the structural term, U_{II} , is about one-tenth of the total energy, as pointed out in the introduction. The non-local term U_{NL} is the same order of

Table 1. contributions to the total energy per ion, U_{tot} , as a function of density in units of the zero-temperature equilibrium density, ρ_0 . The structure, equilibrium lattice constant a and pseudopotential parameters (where A_i are the well depths in rydbergs and R_i the well radii in atomic units) assumed for each metal are indicated at the head of each part of the table. See text (section 4.1) for definitions of each contribution. All energies are in eV.

(a) Lithium, Li: FCC, $a = 4.382 \text{ \AA}$, $A_0 = -0.70$, $A_1 = A_2 = -1.32$, $R_1 = R_2 = 2.38$.

ρ/ρ_0	U_L	U_{NL}	U_0	U_{II}	U_{tot}	U_{HO}	\bar{U}_{tot}
0.80	-7.6028	0.2915	-7.3113	-0.4037	-7.7151	-0.1307	-7.8458
0.90	-7.7342	0.3480	-7.3862	-0.4175	-7.8037	-0.0653	-7.8691
0.95	-7.7976	0.3772	-7.4204	-0.4212	-7.8415	-0.0327	-7.8742
0.98	-7.8351	0.3951	-7.4400	-0.4225	-7.8625	-0.0131	-7.8756
0.99	-7.8475	0.4011	-7.4464	-0.4228	-7.8692	-0.0065	-7.8757
1.00	-7.8598	0.4071	-7.4527	-0.4230	-7.8757	0.0000	-7.8757
1.01	-7.8723	0.4132	-7.4591	-0.4231	-7.8822	0.0065	-7.8757
1.02	-7.8845	0.4193	-7.4652	-0.4232	-7.8885	0.0131	-7.8754
1.05	-7.9210	0.4376	-7.4834	-0.4231	-7.9065	0.0327	-7.8738
1.10	-7.9809	0.4687	-7.5122	-0.4217	-7.9339	0.0653	-7.8686
1.20	-8.0976	0.5324	-7.5652	-0.4150	-7.9801	0.1307	-7.8495
1.30	-8.2106	0.5982	-7.6124	-0.4037	-8.0161	0.1960	-7.8201
1.40	-8.3202	0.6657	-7.6545	-0.3887	-8.0432	0.2614	-7.7818
1.50	-8.4265	0.7348	-7.6917	-0.3706	-8.0623	0.3268	-7.7355
1.60	-8.5296	0.8054	-7.7242	-0.3499	-8.0741	0.3921	-7.6820
1.70	-8.6300	0.8773	-7.7527	-0.3270	-8.0797	0.4575	-7.6222
1.80	-8.7275	0.9504	-7.7771	-0.3023	-8.0794	0.5229	-7.5565
1.90	-8.8224	1.0246	-7.7979	-0.2760	-8.0739	0.5882	-7.4857
2.00	-8.9147	1.0997	-7.8150	-0.2485	-8.0634	0.6536	-7.4099

(b) Sodium, Na: BCC, $a = 4.227 \text{ \AA}$, $A_0 = A_1 = -0.255$, $A_2 = -0.50$, $R_0 = 1.87$, $R_1 = R_2 = 1.93$.

ρ/ρ_0	U_L	U_{NL}	U_0	U_{II}	U_{tot}	U_{HO}	\bar{U}_{tot}
0.80	-6.5870	-0.0070	-6.5940	-0.1916	-6.7857	-0.0625	-6.8482
0.90	-6.6494	-0.0083	-6.6578	-0.1863	-6.8441	-0.0312	-6.8753
0.95	-6.6786	-0.0090	-6.6876	-0.1785	-6.8661	-0.0156	-6.8817
0.98	-6.6955	-0.0094	-6.7050	-0.1722	-6.8772	-0.0063	-6.8835
0.99	-6.7011	-0.0096	-6.7107	-0.1699	-6.8806	-0.0031	-6.8837
1.00	-6.7066	-0.0097	-6.7163	-0.1674	-6.8838	0.0000	-6.8838
1.01	-6.7121	-0.0099	-6.7220	-0.1649	-6.8868	0.0031	-6.8837
1.02	-6.7175	-0.0100	-6.7275	-0.1622	-6.8897	0.0062	-6.8834
1.05	-6.7336	-0.0104	-6.7440	-0.1534	-6.8974	0.0156	-6.8817
1.10	-6.7596	-0.0111	-6.7707	-0.1364	-6.9071	0.0312	-6.8759
1.20	-6.8090	-0.0126	-6.8216	-0.0943	-6.9159	0.0625	-6.8535
1.30	-6.8556	-0.0141	-6.8697	-0.0421	-6.9118	0.0937	-6.8180
1.40	-6.8996	-0.0156	-6.9152	0.0194	-6.8958	0.1250	-6.7708
1.50	-6.9414	-0.0172	-6.9585	0.0895	-6.8690	0.1562	-6.7128
1.60	-6.9812	-0.0187	-6.9999	0.1675	-6.8324	0.1875	-6.6449
1.70	-7.0192	-0.0203	-7.0395	0.2529	-6.7865	0.2187	-6.5678
1.80	-7.0556	-0.0219	-7.0774	0.3452	-6.7322	0.2500	-6.4823
1.90	-7.0906	-0.0235	-7.1140	0.4440	-6.6700	0.2812	-6.3888
2.00	-7.1241	-0.0250	-7.1491	0.5487	-6.6004	0.3124	-6.2880

Table 1—continued.

(c) Aluminium, Al: FCC, $a = 4.033 \text{ \AA}$, $A_0 = A_1 = -2.22$, $A_2 = -6.70$, $R_0 = 1.45$, $R_1 = R_2 = 1.31$.

ρ/ρ_0	U_L	U_{NL}	U_0	U_{II}	U_{tot}	U_{HO}	\bar{U}_{tot}
0.80	-59.2561	0.3984	-58.8577	0.1166	-58.7410	-0.2348	-58.9759
0.90	-59.6221	0.4848	-59.1374	0.1841	-58.9533	-0.1174	-59.0708
0.95	-59.7960	0.5304	-59.2656	0.2295	-59.0361	-0.0587	-59.0948
0.98	-59.8958	0.5586	-59.3373	0.2605	-59.0768	-0.0235	-59.1003
0.99	-59.9298	0.5681	-59.3617	0.2716	-59.0901	-0.0117	-59.1019
1.00	-59.9623	0.5777	-59.3846	0.2829	-59.1018	0.0000	-59.1018
1.01	-59.9955	0.5873	-59.4082	0.2945	-59.1136	0.0118	-59.1018
1.02	-60.0271	0.5970	-59.4301	0.3064	-59.1236	0.0235	-59.1002
1.05	-60.1238	0.6265	-59.4972	0.3443	-59.1530	0.0587	-59.0942
1.10	-60.2789	0.6769	-59.6019	0.4136	-59.1884	0.1174	-59.0710
1.20	-60.5755	0.7823	-59.7931	0.5763	-59.2168	0.2348	-58.9820
1.30	-60.8499	0.8937	-59.9562	0.7700	-59.1862	0.3522	-58.8340
1.40	-61.1117	1.0108	-60.1009	0.9959	-59.1050	0.4697	-58.6353
1.50	-61.3572	1.1335	-60.2237	1.2524	-58.9713	0.5870	-58.3843
1.60	-61.5897	1.2617	-60.3280	1.5393	-58.7887	0.7044	-58.0842
1.70	-61.8093	1.3952	-60.4141	1.8558	-58.5583	0.8219	-57.7364
1.80	-62.0170	1.5339	-60.4830	2.2009	-58.2822	0.9393	-57.3429
1.90	-62.2128	1.6777	-60.5351	2.5734	-57.9616	1.0567	-56.9049
2.00	-62.3985	1.8265	-60.5720	2.9734	-57.5986	1.1741	-56.4245

(d) Potassium, K: BCC, $a = 5.233 \text{ \AA}$, $A_0 = A_1 = -0.32$, $A_2 = -1.80$, $R_0 = 2.65$, $R_1 = R_2 = 3.08$.

ρ/ρ_0	U_L	U_{NL}	U_0	U_{II}	U_{tot}	U_{HO}	\bar{U}_{tot}
0.80	-5.4940	-0.0133	-5.5073	-0.1896	-5.6969	-0.0610	-5.7579
0.90	-5.5501	-0.0126	-5.5627	-0.1891	-5.7517	-0.0305	-5.7822
0.95	-5.5770	-0.0119	-5.5888	-0.1837	-5.7725	-0.0152	-5.7878
0.98	-5.5927	-0.0113	-5.6040	-0.1790	-5.7830	-0.0061	-5.7891
0.99	-5.5979	-0.0111	-5.6091	-0.1772	-5.7863	-0.0031	-5.7893
1.00	-5.6033	-0.0109	-5.6142	-0.1753	-5.7895	0.0000	-5.7895
1.01	-5.6084	-0.0107	-5.6191	-0.1733	-5.7924	0.0030	-5.7893
1.02	-5.6136	-0.0105	-5.6241	-0.1711	-5.7952	0.0061	-5.7891
1.05	-5.6291	-0.0097	-5.6389	-0.1640	-5.8028	0.0152	-5.7876
1.10	-5.6547	-0.0083	-5.6629	-0.1499	-5.8128	0.0305	-5.7824
1.20	-5.7050	-0.0046	-5.7096	-0.1142	-5.8238	0.0610	-5.7628
1.30	-5.7543	0.0002	-5.7541	-0.0690	-5.8231	0.0914	-5.7317
1.40	-5.8030	0.0061	-5.7969	-0.0156	-5.8125	0.1219	-5.6906
1.50	-5.8519	0.0132	-5.8387	0.0453	-5.7934	0.1524	-5.6410
1.60	-5.8999	0.0214	-5.8785	0.1130	-5.7655	0.1828	-5.5826
1.70	-5.9484	0.0309	-5.9175	0.1866	-5.7309	0.2134	-5.5175
1.80	-5.9966	0.0416	-5.9550	0.2658	-5.6892	0.2438	-5.4454
1.90	-6.0451	0.0536	-5.9915	0.3498	-5.6417	0.2743	-5.3674
2.00	-6.0941	0.0668	-6.0273	0.4380	-5.5893	0.3048	-5.2845

Table 2. Contributions to the total energy of Al per ion, U_0 , U_{II} and U_{tot} , as functions of density when the pseudopotential well depths are varied with the density. The energies are in eV. The columns headed A_0 , A_1 and A_2 are the well depths in rydbergs.

ρ/ρ_0	A_0	A_1	A_2	U_0	U_{II}	U_{tot}
0.96	2.236	2.236	6.750	-59.3410	0.2411	-59.0999
0.98	2.228	2.228	6.725	-59.3630	0.2613	-59.1018
1.00	2.220	2.220	6.700	-59.3846	0.2829	-59.1018
1.02	2.212	2.212	6.675	-59.4059	0.3059	-59.1000
1.04	2.204	2.204	6.650	-59.4267	0.3303	-59.0964

magnitude as U_{II} and increases rapidly with density, so that it will make a significant contribution to the pressure. The results for U_{tot} in table 1 show that the minimum in U_{tot} occurs at $\rho/\rho_0 = 1.7$ for Li and $\rho/\rho_0 = 1.2$ for Na, Al and K. In all cases the densities are much higher than the observed low-temperature values. This disagreement is surprising in view of the fact that the calculation is entirely first-principles and that our formalism includes important details such as the non-local pseudopotential contribution to U_0 . We believe that the origin of this discrepancy is the density dependence of terms in the total energy beyond second order in the pseudopotential. In the following paragraphs we explain how the discrepancy arises in the context of the DRT pseudopotential and why there will be similar difficulties for all pseudopotential calculations that only go to second order.

For the DRT pseudopotential, the high-order terms in the total energy are important because of the way in which the pseudopotential parameters were derived. This is briefly as follows. First of all, the charge density induced around an isolated ion in an infinite electron gas was calculated self-consistently from density-functional theory. Here the density of the electron gas corresponded to the observed zero-temperature value for the metal. Then the same quantity was evaluated to first order in perturbation theory using a pseudopotential formally equivalent to the full ionic potential used in the first calculation. Finally, the pseudopotential parameters were adjusted so as to bring the first-order calculation into coincidence with the full non-linear calculation. The idea was to force the perturbation theory approach to reproduce the correct isolated-ion charge density. By doing this, the effect of an entire series of higher-order terms non-linear in the charge density was folded into the pseudopotential parameters. Clearly, in principle the DRT pseudopotential parameters must depend on the density of the electron gas. However, it was always argued that this effect would be negligibly small and could hence be ignored. The successful prediction of the temperature dependence of electron transport properties, phonons and defect behaviour (e.g. Taylor 1982, Jacucci *et al* 1981) appeared to vindicate this assumption. Nevertheless, we find that the density dependence of total energy is in fact sensitive to the density dependence of the pseudopotential parameters from the higher non-linear corrections that have been folded into them.

In table 2 we present results for U_0 , U_{II} and U_{tot} for $0.96 \leq \rho/\rho_0 \leq 1.04$ for Al by allowing the pseudopotential wells to deepen by 0.37% for every 2% decrease in the density. The pseudopotential well depths used are also included in the table. As can be seen, the very small changes in the pseudopotential as a function of the density are

Table 3. Values of μ for Li, Na, Al and K.

	Li	Na	Al	K
μ	0.0777	0.0451	0.1285	0.0545

sufficient to equilibrate the system at the correct density. Particularly interesting is the fact that a comparison with table 1(c), where there is no density dependence in the pseudopotential, shows that the change in U_0 is more than an order of magnitude larger than the change in U_{II} . We conclude that the size of the density dependence of the pseudopotential needed to achieve equilibrium is too small to have any impact on the pair potential and hence the pair potential can be calculated with density-independent pseudopotential parameters.

It is beyond the scope of this paper to repeat the DRT calculations at different electron-gas densities, so we have no way of estimating the magnitude of the density dependence of the DRT pseudopotential parameters. We can, however, obtain a rough guess from the fact that the difference between linear and non-linear charge densities calculated by DRT for Al, Mg, Na and K (all of which have similar core structures) appears to increase steadily with decreasing electron density. Such behaviour is not surprising since the kinetic energy becomes less and less dominant with decreasing density, so that the pseudopotential parameters would have to be strengthened as the density decreases. This concurs with the results in table 2.

Rather than find the exact density dependence of the pseudopotential parameters to achieve the observed low-temperature equilibrium volume, we can utilize the fact that only the density dependence of the volume term U_0 is significantly affected by the changes in the pseudopotential parameters. Hence we can simply add a correction term U_{HO} to U_0 , which takes the form

$$U_{HO} = \mu Ze^2 (\rho/\rho_0 - 1)/(4\pi\epsilon_0 r_{WS}). \quad (4.3)$$

Here r_{WS} is the Wigner–Seitz sphere radius and μ is a dimensionless parameter adjusted to give the correct equilibrium density. We have chosen this form because of its very simple density dependence and because $Ze^2/(4\pi\epsilon_0 r_{WS})$ is a natural energy unit of the system. The value of μ is fixed to force the derivative of \bar{U}_{tot} with respect to the density to be zero at $\rho/\rho_0 = 1$, where \bar{U}_{tot} is defined in equations (4.1) and (4.2) above. \bar{U}_{tot} is shown as the final column table 1 and the values of μ for Li, Na, Al and K are given in table 3.

Finally in this subsection, we emphasize that we would expect that a term like U_{HO} would have to be added to U_0 for all pseudopotential calculations of the total energy to second order in pseudopotential theory. Any pseudopotential fitted to an experimental property would have implicitly the same non-linearities as discussed in the context of the DRT potential folded into it. Furthermore, any first-principles pseudopotential calculation that explicitly ignored the effect of the higher-order terms would again need a correction term to equilibrate the system at the observed volume. Note, for example, that Cagin and Ray (1988) included such a correction without any formal justification. It follows, then, that to determine pseudopotential parameters by fitting to the observed equilibrium density is likely to lead to other properties not agreeing with experiment. This is indeed the case for the local pseudopotential of Walker *et al* (1986), which was

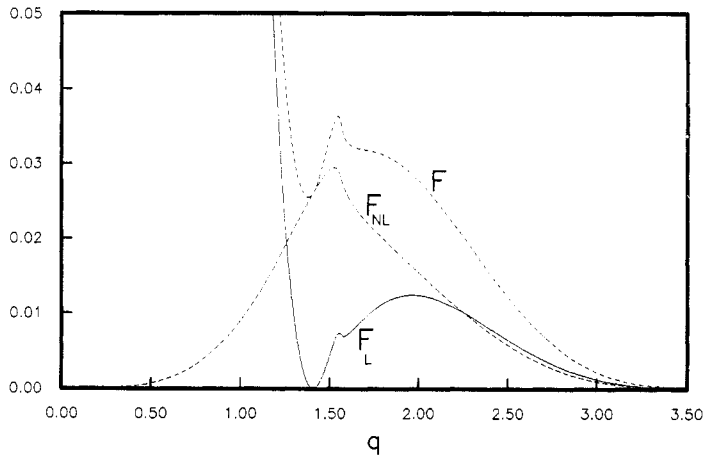


Figure 1. Contributions to the energy-wavenumber characteristic $F(q)$ for Li. The local and non-local contributions, $F_L(q)$ and $F_{NL}(q)$ respectively, are defined in equations (2.14)–(2.16). The wavevector q is in units of $2\pi/a = 0.782k_F$, where a is the low-temperature equilibrium lattice constant for FCC.

fitted to the equilibrium density of Li and gives poor phonon dispersion curves (A B Walker, unpublished).

4.2. Energy-wavenumber characteristic

We would expect Li to be strongly non-local due to the lack of occupied p states in the Li core. In that case, valence electrons in p states will experience the full attractive potential from the ion core as they are not orthogonal to the s-state core electrons. Therefore Li is a good test of the importance of non-locality and accordingly all the calculations in this section have been made for Li. We have plotted $F_L(q)$, $F_{NL}(q)$ and $F(q)$ in figure 1. To obtain these curves we have used the formalism described in section 4.1. Figure 1 shows that $F_{NL}(q)$ dominates at wavevectors around $2k_F$ and will therefore contribute to long-range oscillations in $n(q)$. Reproducing these oscillations in $n(q)$ by fixing the local pseudopotential within an analytic form for the latter is likely to result in a poor description of the transport properties (Taylor 1982). Nevertheless, this does not preclude the possibility that the pair potential is adequately described by the approximation that

$$F(q) \approx F_L(q). \quad (4.4)$$

For a local pseudopotential the matrix element $\langle \mathbf{k} | v_p | \mathbf{k} + \mathbf{q} \rangle$ is independent of \mathbf{k} . Therefore, from equations (2.11) and (2.12), \bar{v}_p^2 is equal to $(\bar{v}_p)^2$ and so $F_{NL}(q)$ is zero. Manninen *et al* (1981) define a local pseudopotential $v_p(q)$ from the equation

$$n(q) = -v_p(q)\chi(q)S(q) \quad (4.5)$$

where $n(q)$ is obtained from a self-consistent calculation of the electron density around an isolated Al nucleus, embedded, in different schemes, in jellium and in a jellium

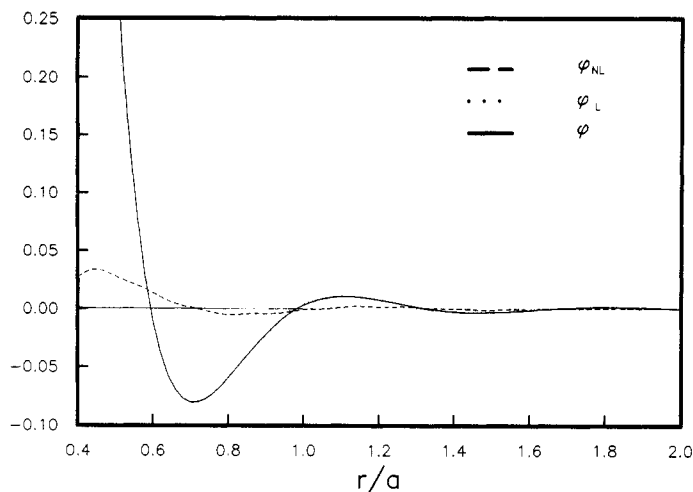


Figure 2. Contributions to the effective pair potential φ for Li. The resulting pair potentials if $F(q) = F_L(q)$ or $F(q) = F_{NL}(q)$, namely φ_L and φ_{NL} respectively, are also shown. The distance r is given in units of the low-temperature equilibrium lattice constant a for FCC, i.e. 4.382 Å.

vacancy. Figure 2 shows $\varphi(r, \rho)$ for Li evaluated from equation (2.24) at the standard density ρ_0 , where the full curve is for $F(q)$ from equation (2.14), the dotted curve from equation (4.4) and the broken curve with $F(q)$ set equal to $F_{NL}(q)$ and $v_c(r) = 0$. The broken curve represents only the non-local contribution to $\varphi(r, \rho)$. The same parameter values and lattice constant as for figure 1 have been adopted. From figure 2 it is apparent that the approximation (4.4) is a good one even for Li. Thus, any properties that depend on the pair potential, such as the phonon dispersion curves, are likely to be well described by a local pseudopotential obtained by Manninen *et al's* (1981) prescription.

If a local pseudopotential is used, it should be chosen carefully. Manninen *et al's* (1981) prescription works for the pair potential because their local pseudopotential reproduces the non-linear charge density around an isolated ion and so, like the pseudopotentials of Dagens *et al* (1975), has non-linear effects in the response of conduction electrons to ionic perturbations folded in. Note that the functional form of $F(q)$ is considerably more complex than that which is generated by an analytic local pseudopotential.

5. Summary and conclusions

Within second-order pseudopotential theory, the total energy U_{tot} of a simple metal may be written as the sum of a 'volume term' U_0 , which depends only on the density ρ of the system, and a structure-dependent term U_{II} , which is itself a sum over density-dependent pair potentials $\varphi(r, \rho)$. We have evaluated U_{tot} for Li, Na, Al and K using the first-principles pseudopotentials of Dagens *et al* (1975), which are constructed to give the correct non-linear charge density for an isolated ion in an infinite electron gas when used to first order in perturbation theory. Our derivation of $U_0(\rho)$ goes beyond that of Finnis (1974) since it includes an extra term due to the non-locality of the pseudopotential (equation (2.22)).

Even with this extra term, we still find that the system equilibrates to a density much higher than observed. We have argued that the origin of this discrepancy lies in the neglect of the density dependence of the higher-than-second-order terms in the total energy, and have shown that a weak density dependence in the pseudopotential is necessary to equilibrate the system at the right density. Of particular importance is the fact that this density dependence has a much bigger impact on $U_0(\rho)$ than on $U_{II}(\rho)$, thereby justifying the neglect of this effect when calculating pair potentials at different densities. An extra term, U_{HO} (equations (4.1)–(4.3)), is included in U_0 with a coefficient adjusted to give the observed equilibrium density, to account for the density dependence of the higher-order terms. It should be noted that such a term is required in all cases where the total energy is calculated to second order in the pseudopotential.

The density dependence of $U_0(\rho)$ and $\varphi(r, \rho)$ is of critical importance in simulations of simple metal properties with the Parrinello and Rahman (1980) variable cell molecular dynamics scheme. To evaluate $\varphi(r, \rho)$ at different densities within that scheme would require large amounts of computer time, particularly since the non-local pseudopotential formulation of the pair potential involves several complicated multidimensional integrals. Consequently, in the following paper, paper II, we have fitted the potentials generated in this paper to a simple analytic form suitable for such a simulation. We have also provided small- and large- q expansions of the integrals (see appendix 1) as well as analytic representations of the most important of them, \bar{L}_0 and \bar{L}_1 (equations (3.8)–(3.13)).

Another important simplification in the evaluation of $\varphi(r, \rho)$ is to use the local density approximation for the local field of the electron–gas dielectric function (Taylor 1978). In appendix 2 we have provided an improved local field (equation (A2.4)) over that suggested by Taylor (1978). This is based on the Vosko *et al* (1980) interpolation formula for the Ceperley and Alder (1980) results for the correlation energy of the electron gas.

Finally, we have noted that the energy–wavenumber characteristic, $F(q)$, can be written as the sum of two terms, $F_L(q)$ and $F_{NL}(q)$, where the latter is identically zero for a local pseudopotential. This result justifies the approach of Manninen *et al* (1981), who determined a pair potential directly from the isolated-ion charge density in an electron gas without going through the intermediate stage of constructing an analytic pseudopotential. We have pointed out that $F_L(q)$ is considerably more complex than the form that is derived from an analytic local pseudopotential.

Acknowledgments

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Appendix 1. Expansions for non-local integrals and $F(q)$

Here we list the expressions for the non-local integrals \bar{L}_i and \bar{L}_{ij} , where $i, j = 0, 1$, which appear in the local ($F_L(q)$) and non-local ($F_{NL}(q)$) components of the energy–wavenumber characteristic, equations (3.6) and (3.7). We also give the expansions of

these integrals in powers of q'^2 and $1/q'^2$ ($q' = q/k_F$). The expansions for \bar{L}_0 and \bar{L}_1 are also used to generate the analytic representations of these functions discussed in section 3, and to fit a Padé approximant to $F(q)$ from which we have obtained an analytic expression for the effective pair potential and the band-structure term in U_0 (see paper II).

The definitions of the non-local integrals are as follows: for $q' \leq 2$

$$\bar{L}_i = (1/f_0) \int_0^1 dx/x \int_0^1 dt k' K_i(k'_+, k'_-, R') [\mathbf{k}_+ \cdot \mathbf{k}_- / (k_+ k_-)]^i \quad (\text{A1.1})$$

$$k' = (t - \frac{1}{2})q'x + [1 - q'^2(x^2 - 1)/4]^{1/2} \quad (\text{A1.2})$$

and for $q' \geq 2$

$$\bar{L}_i = [2/(f_0 q')] \int_{\chi_M}^1 dx [1 + q'^2(x^2 - 1)/4]^{1/2} \int_0^1 dt k' K_i(k'_+, k'_-, R') [\mathbf{k}_+ \cdot \mathbf{k}_- / (k_+ k_-)]^i \quad (\text{A1.3})$$

$$k' = q'x/2 + (2t - 1)[1 - q'^2(x^2 - 1)/4]^{1/2}. \quad (\text{A1.4})$$

Here

$$\mathbf{k}'_{\pm} = \mathbf{k}' \pm \mathbf{q}'/2 = \mathbf{k}_{\pm}/k_F \quad (\text{A1.5})$$

$$\chi_M = (1 - 4/q'^2)^{1/2} \quad (\text{A1.6})$$

$$K_0(k_1, k_2, R) = [\sin(k_2 R) \cos(k_1 R)/k_2 - \sin(k_1 R) \cos(k_2 R)/k_1] / (k_2^2 - k_1^2) \quad (\text{A1.7})$$

$$K_1(k_1, k_2, R) = R[j_1(k_2 R) \sin(k_1 R) - j_1(k_1 R) \sin(k_2 R)] / (k_2^2 - k_1^2) \quad (\text{A1.8})$$

where $j_l(x)$ is the spherical Bessel function of order l . The non-local integrals \bar{L}_{ij} are defined in a similar way to \bar{L}_i except that $K_i(k'_+, k'_-, R') [\mathbf{k}_+ \cdot \mathbf{k}_- / (k_+ k_-)]^i$ is replaced by $K_i(k'_+, k'_-, R') K_j(k'_+, k'_-, R') [\mathbf{k}_+ \cdot \mathbf{k}_- / (k_+ k_-)]^{i+j}$ in the integrands.

For low q we have obtained the expansions below. Here $c_i = \cos(iR')$, $s_i = \sin(iR')$, $c' = c_2 - 1$ and $s' = s_2 - 2R'$. If $x = q'^2$,

$$\begin{aligned} \bar{L}_0 = \sum_i E_0(i)x^i = & -s'/4 + x[(R'^2 - 3)s' + 2R'c']/72 - x^2[(9R'^4 - 106R'^2 \\ & + 165)s' - 158R'c' + R'^3(36c' - 96)]/21600 \end{aligned} \quad (\text{A1.9})$$

$$\begin{aligned} \bar{L}_{00} - (\bar{L}_0)^2 = \sum_i E_{00}(i)x^i = & x[(3s' - 2c'R')^2]/576 \\ & + x^2\{(224R'^4 - 3828R'^2 + 8685)s'^2 + [576R'^5 \\ & + (3488c' - 3888)R'^3 - 13524c'R']s' + 576R'^6 \\ & + (3168 - 432c')R'^4c' + 5300c'^2R'^2\}/518400 \end{aligned} \quad (\text{A1.10})$$

$$\begin{aligned} \bar{L}_1 = \sum_i E_1(i)x^i = & (R's_2 + 2c_2 + 2R'^2 - 2)/(4R') \\ & - x[(R'^2 - 3)s_2 + 4R'c_2 + 2R'^3 + 2R']/72 \\ & + x^2[(9R'^4 - 154R'^2 + 165)s_2 + (54R'^3 - 262R')c_2 \\ & + 18R'^5 - 50R'^3 - 68R']/21600 \end{aligned} \quad (\text{A1.11})$$

$$\begin{aligned} \bar{L}_{11} - (\bar{L}_1)^2 = \sum_i E_{11}(i)x^i = & -x[(28R'^3 - 112R')s_4 + (-4R'^4 + 81R'^2 - 64)c_4 \\ & + (-112R'^3 + 224R')s_2 + (32R'^4 - 192R'^2 + 256)c_2 - 36R'^4 \\ & + 111R'^2 - 192]/(1152R'^2) + x^2[(6112R'^5 - 75444R'^3 + 159168R')s_4 \\ & + (-656R'^6 + 27368R'^4 - 137349R'^2 + 91200)c_4 + (640R'^7 - 34688R'^5 \\ & + 217152R'^3 - 318336R')s_2 + (7168R^6 - 99200R'^4 + 357120R'^2 \\ & - 364800)c_2 + 640R'^8 - 16208R'^6 + 98496R'^4 - 219771R'^2 \\ & + 273600]/(1036800R'^2) \end{aligned} \quad (\text{A1.12})$$

$$\begin{aligned} \bar{L}_{01} - \bar{L}_0\bar{L}_1 = \sum_i E_{01}(i)x^i = & x[(20R'^2 - 24)s_4 + (-4R'^3 + 37R')c_4 + (32R'^2 + 48)s_2 \\ & + 32R'c_2 + 28R'^3 - 69R']/(1152R') - x^2[(4800R'^4 - 35844R'^2 + 27072)s_4 \\ & + (-656R'^5 + 16936R'^3 - 45417R')c_4 + (5568R'^4 - 15936R'^2 - 54144)s_2 \\ & + (-640R'^5 + 12416R'^3 - 24576R')c_2 - 640R'^7 + 11952R'^5 - 50016R'^3 \\ & + 69993R']/(1036800R') \end{aligned} \quad (\text{A1.13})$$

$$\begin{aligned} M_L = \sum_i E_M(i)x^i = & -1 + x[R'^2(2A'_2R' + 3)]/6 - x^2[R'^4(4A'_2 + 5)]/120 \\ & + x^3[R'^6(6A'_2 + 7)]/5040 \end{aligned} \quad (\text{A1.14})$$

$$\begin{aligned} \chi = \sum_i E_C(i)x^i = & 1 + x[\gamma - 1/(4\lambda)] + x^2\{[\gamma - 1/(4\lambda)]^2 - 1/(48\lambda)\} - x^3\{[\gamma - 1/(4\lambda)]^3 \\ & + [\gamma - 1/(4\lambda)]/(24\lambda) + 1/(360\lambda)\}. \end{aligned} \quad (\text{A1.15})$$

Let

$$E(i) = E_M(i) + \alpha_0 E_0(i) + 3\alpha_1 E_1(i) \quad (\text{A1.16})$$

$$E_D(i) = \alpha_0^2 E_{00}(i) + 6\alpha_0\alpha_1 E_{01}(i) + 9\alpha_1^2 E_{11}(i) \quad (\text{A1.17})$$

then

$$(1 - F(x))/x = F_1x + F_2x + F_3x^2$$

$$F_1 = 2E(1) - E_C(1) \quad (\text{A1.18})$$

$$F_2 = 2[E(2) + E(1)E_C(1)] - E_C(2) - E(1)^2 - 4\lambda E_D(1) \quad (\text{A1.19})$$

$$\begin{aligned} F_3 = 2\{E(3) + E(1)[E_C(2) - E(2)] + E(2)E_C(1)\} - E_C(1)E(1)^2 - E_C(3) \\ - 4\lambda[E_D(2) - E_D(1)/12]. \end{aligned} \quad (\text{A1.20})$$

For large values of q' the following expressions have been derived:

$$\begin{aligned} \lim_{q' \rightarrow \infty} \bar{L}_0 = & -s'[3 \sin(q'R')/(q'R') - \cos(q'R') \\ & - 8R'^2 \sin(q'R')/(3q'R')]/(4q'^2R')^2 \end{aligned} \quad (\text{A1.21})$$

and

$$\begin{aligned} \lim_{q' \rightarrow \infty} \bar{L}_i = & -3[s'/4 + R'j_1(q'R') \sin(R')]/j_1(q'R')/(q'R') \\ & + 4[s'/4 + 2R'j_1(q'R') \sin(R')]/j_0(q'R')/(9q'^2). \end{aligned} \quad (\text{A1.22})$$

Appendix 2. Electron-electron interactions

In this appendix we present a very simple approximation to the electron-gas local field

$\varphi_{\text{LF}}(q)$, which works well for most calculations of the physical properties of metals. Taylor (1978) has pointed out the adequacy of the local-density approximation (LDA) to the local field, the LDA being an approximation whereby $\varphi_{\text{LF}}(q)$ is replaced by $\varphi_{\text{LF}}(0)$ for all q . In this paper he suggested the use of $\varphi_{\text{LF}}(0)$ derived from the Nozieres and Pines (1958) approximation to the electron-gas correlation energy. Here we provide a much better representation of the correlation energy based on the work of Vosko *et al* (1980) (VWN), who have provided a detailed analysis of recent work on the electron-gas energy.

The dielectric function for the interacting electron gas can be written in the form

$$\varepsilon(q) = 1 + [e^2/(\varepsilon_0 q^2)]\Pi(q) \quad (\text{A2.1})$$

where the polarizability $\Pi(q)$ is related to $\varphi_{\text{LF}}(q)$ by the expression

$$\Pi(q) = \Pi_0(q)/[1 - e^2 \varphi_{\text{LF}}(q)\Pi_0(q)/\varepsilon_0]. \quad (\text{A2.2})$$

$\Pi_0(q)$ is the polarizability for the non-interacting electron gas. Taylor (1978) has suggested the following approximation for $\varphi_{\text{LF}}(0)$:

$$\varphi_{\text{LF}}(0) = [1 - (1 - \ln 2)\lambda/2]/(4k_{\text{F}}^2) \quad (\text{A2.3})$$

where $\lambda = 1/(\pi a_0 k_{\text{F}}) = r_{\text{S}}/6.064$, a_0 is the Bohr radius and r_{S} is the radius of a sphere containing one electron. In the following we show that a better approximation to $\varphi_{\text{LF}}(0)$ is

$$\varphi_{\text{LF}}(0) = [1 - (1 - \ln 2)\lambda/(1 + r_{\text{S}})^{1/3}]/(4k_{\text{F}}^2). \quad (\text{A2.4})$$

To understand how we reached this conclusion it is useful to remember that $\varphi_{\text{LF}}(0)$ is related to the ground-state energy of the electron gas through the compressibility theorem (see e.g. Geldart and Vosko 1966). Using that theorem, and the well known expressions for the kinetic and exchange energies of the electron gas, it is straightforward to show that

$$\varphi_{\text{LF}}(0) = [1 - (1 - \ln 2)\lambda F_{\text{C}}]/(4k_{\text{F}}^2) \quad (\text{A2.5})$$

where the correlation factor

$$F_{\text{C}} = r_{\text{S}} \partial \bar{E}_{\text{C}}/\partial r_{\text{S}} = (r_{\text{S}}/3) \partial (r_{\text{S}} \partial \bar{E}_{\text{C}}/\partial r_{\text{S}})/\partial r_{\text{S}}. \quad (\text{A2.6})$$

\bar{E}_{C} is related to E_{C} , the correlation energy of the electron gas, by

$$\bar{E}_{\text{C}} = \pi^2 E_{\text{C}}/[2(1 - \ln 2)]. \quad (\text{A2.7})$$

From VWN we obtain

$$r_{\text{S}} \partial \bar{E}_{\text{C}}/\partial r_{\text{S}} = (1 + b_1 x)/P(x) \quad (\text{A2.8})$$

$$(r_{\text{S}}/3) \partial (r_{\text{S}} \bar{E}_{\text{C}}/\partial r_{\text{S}})/\partial r_{\text{S}} = x\{b_1 - (1 + b_1 x)[dP(x)/dx]/2\}/P(x) \quad (\text{A2.9})$$

where

$$P(x) = 1 + b_1 x + b_2 x^2 + b_3 x^3$$

and

$$b_1 = 9.81379, b_2 = 2.882224 \text{ and } b_3 = 0.736411.$$

Note that, using equations (A2.4)–(A2.6),

$$\lim_{r \rightarrow 0} \varphi_{\text{LF}}(0) = [1 + \lambda(1 - \ln 2)]/(4k_{\text{F}}^2). \quad (\text{A2.10})$$

This is precisely the result corresponding to the Gell-Mann and Brueckner (1957) exact expression for E_{C} in the small- r_{S} limit.

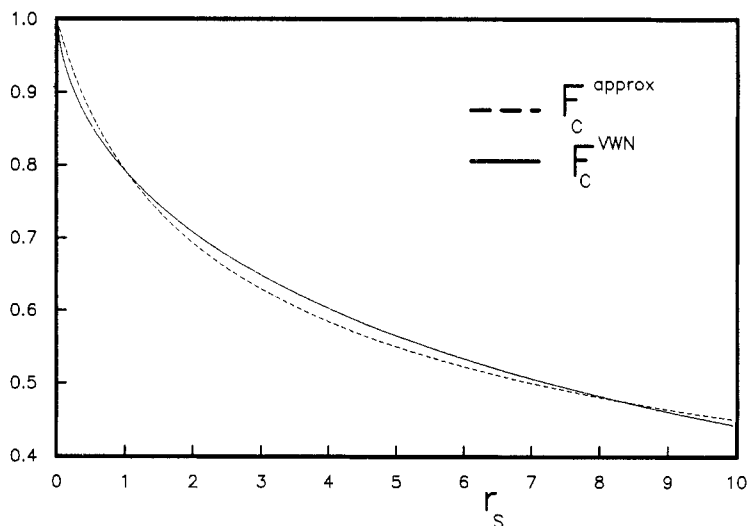


Figure 3. The correlation factor F_C as a function of r_s . The full curve is F_C calculated from the vwn theory, equations (A2.5), and the broken curve is F_C in the approximation in (A2.3). The Nozieres and Pines (1958) approximation to E_C gives $F_C = 0.5$, independent of r_s .

We have calculated F_C as a function of r_s using equations (A2.6)–(A2.9) and plotted the results in figure 3 and compared them with the function $1/(1+r_s)^{1/3}$. As can be seen, the function gives a very good approximation to F_C over the full range of r_s , a significant improvement over the Nozieres–Pines result for which $F_C = \frac{1}{2}$ for all r_s . Hence we conclude that the local field given by equation (A2.4) is distinctly better but just as simple to use as equation (A2.3).

Additionally, it can be shown by integrating equation (A2.5) that (equations (4.3) and (4.4) of vwn) (where E_C is in hartrees):

$$E_C = A[\ln[x^2/X(x)] + (2b/Q) \tan^{-1}[Q/(2x+b)] - [bx_0/X(x)]\{\ln[(x-x_0)^2/X(x)] + 2[(b+2x_0)/Q] \tan^{-1}[Q/(2x+b)]\}] \quad (\text{A2.11})$$

where

$$A = (1 - \ln 2)/\pi^2 \quad (\text{A2.12})$$

$$x = (r_s)^{1/2} \quad (\text{A2.13})$$

$$X(x) = x^2 + bx + c \quad (\text{A2.14})$$

$$Q = (4c - b^2)^{1/2} \quad (\text{A2.15})$$

$$x_0 = -0.409286 \quad b = 13.0720 \quad c = 42.7198. \quad (\text{A2.16})$$

Equation (A2.11) is used for the correlation contribution to the exchange–correlation energy $E_{xc}[n_0]$ in equation (2.19). Using the definition of F_C in terms of the derivatives

of E_C with respect to r_s , it can also be shown that the term in (2.19) which varies as the compressibility of the homogeneous electron gas (energy in hartrees) is

$$0.5Z\Omega^2\partial^2U_{EG}/\partial\Omega^2 = 0.5Z\{1 - \lambda[1 + \lambda(1 - \ln 2)F_C]\}k_F^2/3. \quad (\text{A2.17})$$

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