Binding in pair potentials of liquid simple metals from nonlocality in electronic kinetic energy

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An explicit expression is obtained for the pair potential $\phi(R)$ in liquid simple metals from low-order density-gradient theory when the superposition of single-center displaced charges is employed. Corrections are thereby explicitly exhibited to the local Thomas-Fermi result $\phi_{\rm TF}(R)$ from second- and fourth-order inhomogeneity corrections $\Delta T_2(R)$ and $\Delta T_4(R)$ to the Thomas-Fermi electronic kinetic-energy change $\Delta T_{\rm TF}(R)$. The important point to emphasize is that, in each order, the potential $V(R/2)$ and displaced charge $\Delta(R/2)$ of a single screened ion at the midpoint of the metallic bond completely determines the pair potential in the density-gradient theory. These approximate results are illustrated by explicit calculations on liquid Na and liquid Be near their respective freezing points. While the pair potentials obtained by including $\Delta T_2(R)+\Delta T_4(R)$ are major improvements over the linear response result, the remaining nonlocal corrections to the total kinetic-energy change $\Delta T(R)$ are substantial, as again demonstrated by explicit results for Na and Be. The importance of further study of a possible functional relation between $\Delta T(R)-\Delta T_{\rm TFG}(R)$ and the potential $V(R/2)$ at the midpoint of the metallic bond is finally emphasized.

I. INTRODUCTION

The interaction between a pair of test charges Ze in a metallic medium was studied by means of the linearized Thomas-Fermi (TF) method, the latter being the forerunner of density-functional theory, in the early work of Alfred and March.[1] Their result was, from the linear equation for the screened potential V,

$$\nabla^2 V = q^2 V, \quad q^2 = \frac{4k_f}{\pi a_0}, \quad \bar{n} = \frac{k_f^3}{3\pi^2} \tag{1.1}$$

with q^{-1} the TF screening length and k_f the Fermi wave number, that the two-center potential is the superposition

$$V = V_1 + V_2 \tag{1.2}$$

of the screened potentials centered on the charges 1 and 2, and the total displaced charge $\Delta = n - \bar{n}$ was similarly obtained by superposition of one-center densities. This superposition property lies at the heart also of the present study. The result for the pair interaction $\phi(R)$ for the two test charges Z at separation R was

$$\phi(R) = \frac{Z^2}{R}\exp(-qR) . \tag{1.3}$$

This is simply the interaction of the second charge Z with the screened potential $V(R) = -Z\exp(-qR)/R$ of the first charge.

Corless and March[2] subsequently generalized the linear TF theory[1] and demonstrated that the pair interaction $\phi(R)$ was still

$$\phi(R) = -ZV(R) , \tag{1.4}$$

but that the screened potential $V(R)$ must now be calculated from the equation[3]

$$\nabla^2 V(r) = \frac{2k_f^2}{\pi^2}\int \frac{V(\mathbf{r}')j_1(2k_f|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|^2} ; \tag{1.5}$$

$j_1(x) = (\sin x - x\cos x)/x^2$. This reduces to Eq. (1.1) only for such slowly varying potentials that $V(\mathbf{r}')$ inside the integral in Eq. (1.5) can be replaced by $V(r)$, an approximation which is too primitive to apply to liquid simple metals. Unlike the semiclassical theory based on Eq. (1.1), Eq. (1.5) leads to binding. The **k**-space solution is equivalent to the use of the Lindhard[4] dielectric function, discussed also by Langer and Vosko.[5]

In the present paper, generalization of the above results will be affected in a number of directions, namely, by the following.

(i) Corrections of the TF result (1.1) by adding the lowest-order density-gradient correction $t_2 = (\lambda/8)(\nabla n)^2/n$ to the TF kinetic-energy density. The next-order correction t_4 will also be included.

(ii) Incorporating exchange and correlation, albeit approximately, into the theory at local-density level.

(iii) Demonstrating that same incorporation of single-center nonlinearity can be made in the local-density functional theory.

(iv) Interpretation of $\phi(R)$ in all cases as a sum of local plus nonlocal pieces,

$$\phi(R) = \phi_{\rm loc}(R) + \phi_{\rm nloc}(R) . \tag{1.6}$$

Anticipating one of the important results to be presented in the present paper, let us merely note at this stage from Eqs. (1.3) and (1.4) that, with $V(R) = -Z\exp(-qR)/R$,

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$$\phi_{\rm loc}(R)=\frac{R}{4}\left[V\left[\frac{R}{2}\right]\right]^2 . \tag{1.7}$$

This formula will be shown to be more general than the linear TF method from which it has just been derived. It evidently expresses the local form of the pair potential solely in terms of the electrostatic potential of one screened charge at the midpoint of the metallic bond. Further, Eq. (1.7) shows that the local form is always repulsive, which is related to what is nowadays referred to as Teller's theorem,[6] namely, that binding is not possible in a local (TF) theory.

Given the result (1.7), it is then obvious that the difficult part of the problem of constructing realistic pair potentials $\phi(R)$ is to judiciously approximate the nonlocal contribution in Eq. (1.6) and the main aim of the present work is to discuss this point.

Therefore, to gain initial insight, let us turn immediately to correct the linear TF theory based on Eqs. (1.1)–(1.3) by adding the lowest-order gradient correction to the TF kinetic-energy density.

II. PAIR POTENTIALS IN LINEAR RESPONSE THEORY WITH LOWEST-ORDER GRADIENT CORRECTION

Following the pioneering work of von Weizäcker,[7] one writes the most elementary nonlocal correction to the TF kinetic-energy density in terms of the electron density $n(\mathbf{r})$ in the form

$$t_{\rm TFG}^{(1)}=t_{\rm TF}+\frac{\lambda}{8}\frac{(\nabla n)^2}{n} , \tag{2.1}$$

where $t_{\rm TF}=\frac{3}{10}(3\pi^2)^{2/3}n^{5/3}$. Then, for von Weizsäcker's choice of λ, namely unity, March and Murray[8] converted the resulting density-functional Euler equation to a Schrödinger equation by the substitution

$$\psi=n^{1/2} . \tag{2.2}$$

After linearization of the Euler equation, they were able to solve it self-consistently together with the Poisson equation. As shown in the Appendix, a completely general solution can be obtained for arbitrary values of λ, and the final result is

$$\phi_{\rm TFG}^{(1)}(R)=\frac{1}{4}R\left\{\left[V\left[\frac{R}{2}\right]\right]^2-\gamma^2\left[\Delta\left[\frac{R}{2}\right]\right]^2\right\} , \tag{2.3}$$

where

$$\Delta=n(r)-\bar{n} \tag{2.4}$$

is the displaced electron density and γ^2 is given by

$$\gamma^2=\lambda\frac{\pi}{\bar{n}} . \tag{2.5}$$

The derivation of Eq. (2.3) is carried out in reciprocal space, using the Fourier transform of the response function associated with the kinetic-energy functional in Eq. (2.1).

In the linear response formalism invoked above, $\phi=\phi_{\rm LR}=-ZV$, V and Δ are intrinsic single-center quantities, independent of any two-center model. It is surprising to see that Eq. (2.3), a relation between these quantities, anticipates on the physical picture of binding, where the pair interaction is determined by properties at the midpoint of the bond.

The important points to stress about the nonlocal contribution proportional to $R[\Delta(R/2)]^2$ to the pair potential (2.3) are the following.

(i) It is always attractive; i.e., the nonlocality in the kinetic energy tends to bind the charged centers, though for some choices of λ it is easy to show from the Appendix that the pair potential remains repulsive everywhere.

(ii) As with the local contribution to $\phi_{\rm TFG}(R)$ in Eq. (1.7), the nonlocal contribution $R[\Delta(R/2)]^2$ depends only on a property at the midpoint of the metallic bond.

Naturally, one must not assume that Eq. (2.3) is precise: it is valid within the lowest-order density-gradient treatment. Much of the ensuing discussion will focus on the way Eq. (2.3), plus its extension to include the next-order density-gradient correction T_4 to the kinetic energy (see Sec. IV below), can most fruitfully be converted into realistic information about the true pair interaction $\phi(R)$ in liquid simple metals. With this as the main focal point, it is worthwhile next to introduce the total valence screening charge, $Q(R)$ say, inside a sphere of radius R, and to relate this quantity to $\phi(R)$.

III. TOTAL SCREENING CHARGE $Q(R)$ RELATED TO PAIR INTERACTION $\phi(R)$ IN LINEAR RESPONSE THEORY

The definition of the total screening charge $Q(R)$ is evidently given in terms of the displaced charge $\Delta(r)$ by

$$Q(r)=\int_0^r\Delta(r)4\pi r^2dr . \tag{3.1}$$

From Poisson's equation, the potential $V_e(r)$ treated by the valence displaced charge $\Delta(r)$ around say Na^+ or Be^{++} in their own liquid metals is related to $Q(r)$ since

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dV_e}{dr}\right]=-4\pi\Delta(r) \tag{3.2}$$

and hence

$$\frac{dV_e}{dr}=-\frac{Q(r)}{r^2} . \tag{3.3}$$

But as already discussed in Sec. I, in linear response theory $\phi(r)=-ZV(r)$ and hence the turning points of the pair potential occur at positions R_t, i.e., where

$$\frac{dV}{dr}=\frac{dV_e}{dr}-\frac{Z}{r^2}=0 \tag{3.4}$$

or

$$Q(R_t)=Z . \tag{3.5}$$

Evidently a necessary, though not sufficient, condition for Eq. (3.5) to be satisfied is that $\Delta(r)$ oscillates. To illustrate Eq. (3.5), we have plotted in Fig. 1 $Q(R)$ versus R for liquid Na near freezing using our earlier results.[9] Evi-

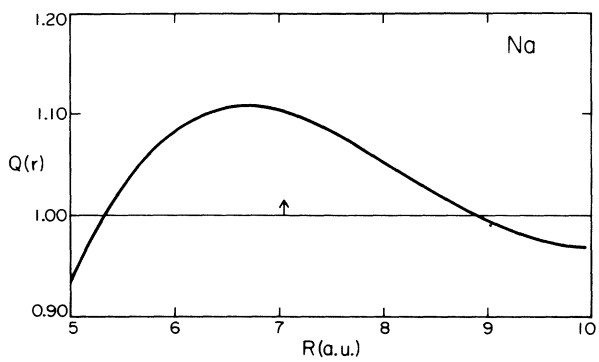

FIG. 1. Total valence screening charge $Q(R)$ defined in Eq. (3.1), for liquid Na near freezing. $Q(R)$ determines the pair interaction $Q(R)$ through Eq. (3.6) in linear response theory. Arrow denotes position of principal minimum in "exact" pair potential ϕ.

dently since the positions of the insertions of $Q(R)/Z$ with unity do not agree with the turning points of the pair potential $\phi(R)$ that we calculated for liquid Na near freezing, linear response theory must be transcended to faithfully reproduce the Na pair potential. Therefore, we shall return to the TF theory corrected by low-order gradients in a more general discussion of pair binding in liquid metals below. However, to summarize the results of this section; when linear response theory is valid (i.e., when $\phi=\phi_{\rm LR}=-ZV$) the total valence screening charge $Q(R)$ uniquely determines the pair potential $\phi(R)$, defined to tend to zero at infinite separation, by integration of the equation obtained from Eqs. (3.3) and (3.4), namely,

$$\frac{d\phi(R)}{dR}=Z\left[\frac{Q(R)-Z}{R^2}\right], \tag{3.6}$$

where Z is the valence.

IV. SUPERPOSITION OF SINGLE-ION DENSITIES AND THE PAIR INTERACTION FROM DENSITY-FUNCTIONAL THEORY

Having noted the inadequacy of the linear response formula for ϕ in liquid Na near freezing, we now return to a more fundamental discussion, still based on density-functional theory (DFT), of the basis of Eq. (2.3), which so far has been derived within the framework of linear response theory for the single-ion screening.

Here, we still retain the superposition of single-ion displaced charge, but focus then directly on the pair problem, utilizing the symmetry about a plane through the midpoint of the metallic bond, and perpendicular to that bond. By doing so, we shall provide a more fundamental derivation of Eq. (2.3), and shall also be able to extend it to include the higher density-gradient correction T_4, to be defined precisely below, to the kinetic energy in local TF theory.

As before, let us start from the DFT equation for a single ion in the electron gas of density $\bar{n}$. This can be written formally as

$$G'[\Delta+\bar{n}]-G'[\bar{n}]=-V(r)\ , \tag{4.1}$$

where G' is simply a shorthand notation for the functional derivative $\delta G/\delta n(r)$, which in TF theory is simply proportional to $[n(r)]^{2/3}$. Here, the functional $G=T+E_{\rm xc}$ includes exchange and correlation effects in the local density approximation. V is the usual electrostatic potential created by the displaced charge $\Delta(r)$, namely,

$$V=-\frac{Z}{r}+\frac{1}{r}*\Delta\ , \tag{4.2}$$

where the $*$ is simply shorthand for the convolution product.

A. Two-center energy calculation with superposition density

Let us consider two ions at positions $\mathbf{R}_i,\mathbf{R}_j$ and, let us also write $\Delta_i=\Delta(\mathbf{r}-\mathbf{R}_i)$ and $\Delta G(\Delta+\bar{n})=G[\Delta+\bar{n}]-G[\bar{n}]$. Then for the pair interaction ϕ between ions i and j we have

$$\begin{aligned}\phi=&\Delta G[\Delta_i+\Delta_j+\bar{n}]-\Delta G[\Delta_i+\bar{n}]-\Delta G[\Delta_j+\bar{n}]\\&+\left[-\frac{Z}{r_i}\right]\cdot\Delta_j+\left[-\frac{Z}{r_j}\right]\cdot\Delta_i\\&+\tfrac{1}{2}(\Delta_i+\Delta_j)\cdot\frac{1}{r}*(\Delta_i+\Delta_j)\\&-\tfrac{1}{2}\Delta_i\cdot\frac{1}{r}*\Delta_i-\tfrac{1}{2}\Delta_j\cdot\frac{1}{r}*\Delta_j+\frac{Z^2}{R}\ .\end{aligned} \tag{4.3}$$

Next it is to be noted from Eq. (2) that

$$\begin{aligned}ZV(R)&=-\frac{Z^2}{R}+\int\frac{Z}{|\mathbf{r}'-\mathbf{R}|}\Delta(\mathbf{r}')d\mathbf{r}'\\&=-\frac{Z^2}{R}+\int\frac{Z}{r''}\Delta(\mathbf{r}''+\mathbf{R})d\mathbf{r}''\\&=-\frac{Z^2}{R}+\left[\frac{Z}{r_i}\right]*\Delta_j\ .\end{aligned} \tag{4.4}$$

Utilizing Eq. (4.4) in Eq. (4.3), one finds

$$\begin{aligned}\phi=&\Delta G[\Delta_i+\Delta_j+\bar{n}]-\Delta G[\Delta_i+\bar{n}]-\Delta G[\Delta_j+\bar{n}]\\&+\left[-\frac{Z}{r_j}\cdot\Delta_i\right]+\tfrac{1}{2}\Delta_i\cdot\frac{1}{r}*\Delta_j+\tfrac{1}{2}\Delta_j\cdot\frac{1}{r}*\Delta_i-ZV(R)\ ,\end{aligned} \tag{4.5}$$

where the dot means the integral of the product of functions through the whole of space; technically the scalar product.

It is important to note at this point that, if one works with the exact density of the "molecule," written as $\Delta_i+\Delta_j+\rho$, instead of with $\Delta_i+\Delta_j$ in the superposition approximation, then Eq. (4.5) is correct to $O(\rho^2)$, due to the stationary properties of the energy functional. Let us now turn to examine several particular cases.

1. Linear response solid

This means $\Delta_i \ll \bar{n}$ and $\Delta_j \ll \bar{n}$ everywhere. Then one can expand the functionals in the form

$$\Delta G[\Delta_i+\Delta_j+\bar{n}]-\Delta G[\Delta_i+\bar{n}]-\Delta G[\Delta_j+\bar{n}]$$
$$=(\Delta_i+\Delta_j)\cdot G'[\bar{n}]-\Delta_i\cdot G'[\bar{n}]-\Delta_j G'[\bar{n}]$$
$$+O(\Delta_i^2,\Delta_i\Delta_j,\Delta_j^2)=0 \tag{4.6}$$

in first order. Thus Eq. (4.5) then yields

$$\phi=-ZV(R)+\cdots , \tag{4.7}$$

where the ellipsis represents second-order terms, which are

$$\tfrac{1}{2}G''[\bar{n}]\cdot[(\Delta_i+\Delta_j)^2-\Delta_i^2-\Delta_j^2]+\tfrac{1}{2}\Delta_i\cdot V_j+\tfrac{1}{2}\Delta_j\cdot V_i ,$$

but from Eq. (4.1)

$$\Delta_i\cdot G''[\bar{n}]=-V_i ,$$

so that the second-order terms vanish to leave the result

$$\phi_{\rm LR}=-ZV(R)+O(\Delta^3) . \tag{4.8}$$

2. Local density approximation for G

Inside the ion core i, Δ_i is much larger than $\bar{n}$ so that expansion in Δ_i is not permissible. But in this same region, Δ_j is very small compared with $\Delta_i+\bar{n}$ so that one can expand in Δ_j. Next, let us exploit the symmetry about the midpoint of the metallic bond in Eq. (4.5) and replace the integration over the whole of space by twice the integration in the half-space Ω_i containing i, as in Fig. 2.

Then we have

$$\phi+ZV(R)=2(\Delta G[\Delta_i+\Delta_j+\bar{n}]-\Delta G[\Delta_i+\bar{n}]$$
$$-\Delta G[\Delta_j+\bar{n}])+\Delta_i\circ V_j+\Delta_j\circ V_i . \tag{4.9}$$

In Eq. (4.9), the volume integrals appearing in ΔG are now restricted to the half-space Ω_i. Now given the assumption that G is local, one can expand for small Δ_j in the half-space Ω_i, to obtain

$$\phi+ZV(R)=2\{\Delta_j\circ G'[\Delta_i+\bar{n}]-\Delta_j\circ G'[\bar{n}]+O(\Delta_j^2)\}$$
$$+\Delta_i\circ V_j+\Delta_j\circ V_i$$
$$=-\Delta_j\circ V_i+\Delta i\circ V_j+O(\Delta_j^2) \tag{4.10}$$

with the help of Eq. (4.1). It is worth noting that Eq. (4.10) retains the full nonlocality of G around the center i and thus transcends linear response. The integrals in the scalar products of Eq. (4.10) are now restricted to the half-space Ω_i and are denoted by an open circle $\circ$. In the second step of Eq. (4.10), use has again been made of the basic Euler Eq. (4.1). Using $\nabla^2 V=-4\pi\{\Delta-Z\delta\}$ one finds

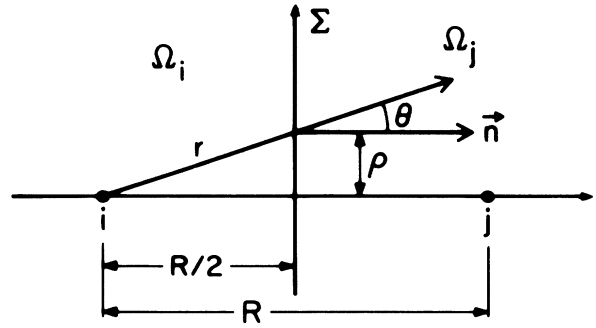

FIG. 2. This defines coordinate system used in calculating pair interaction in local density theory, plus low-order gradients, via surface integrals over the plane Σ, utilizing the symmetry of the homonuclear pair of ions.

$$\phi+ZV(R)=V_j\circ\left[-\frac{\nabla^2 V_i}{4\pi}+Z\delta(\mathbf{r}-\mathbf{R}_i)\right]$$
$$-V_i\circ\left[-\frac{\nabla^2 V_j}{4\pi}+Z\delta(\mathbf{r}-\mathbf{R}_j)\right] . \tag{4.11}$$

Because $\mathbf{R}_j$ is outside Ω_i, the term in $V_i\circ Z\delta(\mathbf{r}-\mathbf{R}_j)$ does not contribute. Therefore

$$\phi+ZV(R)=V(\mathbf{r}-\mathbf{R}_j)\circ Z\delta(\mathbf{r}-\mathbf{R}_i)$$
$$+\frac{1}{4\pi}(V_i\circ\nabla^2 V_j-V_j\circ\nabla^2 V_i) , \tag{4.12}$$

and one is left with an integral over the plane Σ:

$$\phi=\frac{1}{4\pi}\int_\Sigma (V_i\nabla_{\rm n}V_j-V_j\nabla_{\rm n}V_i)ds . \tag{4.13}$$

On this plane one evidently has

$$V_i=V_j ,$$
$$\nabla_{\rm n}V_i=-\nabla_{\rm n}V_j . \tag{4.14}$$

Using the coordinate system of Fig. 2,

$$\phi(R)=\frac{1}{4\pi}\int_0^\infty d\rho\, 2\pi\rho 2V(r)\left[-\frac{dV}{dr}\cos\theta\right] . \tag{4.15}$$

But $\cos\theta=R/2r$, $r^2=R^2/4+\rho^2$ or $r\,dr=\rho\,d\rho$ and hence

$$\phi(R)=-\int_{R/2}^\infty dr\, V(r)\frac{dV}{dr}\frac{R}{2}=\frac{R}{4}\left[V\left[\frac{R}{2}\right]\right]^2+O(\Delta_j^2) . \tag{4.16}$$

Thus, in a considerably more general framework than that employed in Secs. I and II, one regains the local form given in Eqs. (1.7) and (2.3). This establishes then on a more general basis the use of the form (1.7) for the first contribution to the pair potential in Eq. (1.6).

Having discussed fully the local contribution to $\phi(R)$ in Eq. (1.6), it is natural to examine further the status of the nonlocal form in Eq. (2.3). This is done immediately below.

B. Gradient corrections to $\phi_{\rm loc}(R)$

Following the procedure of Sec. II, let us consider next the case when G is given by the usual local leading term, plus a gradient correction

$$T_2=\frac{\lambda}{8}\int\frac{(\nabla n)^2}{n}d\mathbf{r}\ . \tag{4.17}$$

In the pair interaction one then obtains the additional contribution

$$T_2[\Delta_i+\Delta_j+\bar{n}]-T_2[\Delta_i+\bar{n}]-T_2[\Delta_j+\bar{n}]\ .$$

Expanding for small Δ_j the previous line reads

$$\begin{aligned}-\frac{\lambda}{8}\int_{\Omega_i}\frac{|\nabla\Delta_i|^2}{(\Delta_i+\bar{n})^2}\Delta_j d\mathbf{r}-\frac{\lambda}{8}\int_{\Omega_i}\frac{2\nabla\Delta_i\cdot\nabla\Delta_j}{\Delta_i+\bar{n}}d\mathbf{r}+O(\Delta_j^2)\\ =\frac{\lambda}{8}\int_{\Omega_i}\frac{|\nabla\Delta_i|^2}{(\Delta_i+\bar{n})^2}\Delta_j d\mathbf{r}-\frac{\lambda}{4}\int_{\Omega_i}\frac{\nabla^2\Delta_i}{\Delta_i+\bar{n}}\Delta_j d\mathbf{r}\\ +\frac{\lambda}{4}\int\frac{\nabla\Delta_i}{\Delta_i+\bar{n}}\Delta_j ds\ .\end{aligned} \tag{4.18}$$

The first two terms are those which appear in the DFT Euler equation together with the TF term, to give $-\Delta_j\circ V_i$.

The remainder of Eq. (4.18) can be handled again as for the local case, to allow its evaluation on the plane Σ in Fig. 2. The outcome of this is to recover precisely the nonlocal term proportional to $R[\Delta(R/2)]^2$ in Eq. (2.3), which is thereby established on a more general footing.

1. *Inclusion of fourth-order gradient correction*

It will prove important in calculating the well depth of the first minima in the pair potentials of liquid Na (Ref. 9) and Be near freezing to include in the nonlocal part of $\phi(R)$ in Eq. (1.6) the next-order gradient correction t_4 for the kinetic energy.

Following the previous approach, the contribution is that which is associated with the surface integrals in

$$\Delta T_4=T_4[\Delta_i+\Delta_j+\bar{n}]-T_4[\Delta_i+\bar{n}]\ , \tag{4.19}$$

when expanded to first order in Δ_j. $T_4[\Delta_j+\bar{n}]$ does contribute to first order in Δ_j. Writing

$$d=\frac{1}{540}\frac{1}{(2\pi)^{3/2}}\ , \tag{4.20}$$

the form of t_4 calculated by Hodges[10] then yields

$$\begin{aligned}\Delta T_4=2d\int_{\Omega_i}\nabla^2\Delta_j\left[\frac{2\nabla^2\Delta_i}{(\Delta_i+\bar{n})^{5/3}}-\frac{(\frac{9}{8})(\nabla\Delta_i)^2}{(\Delta_i+\bar{n})^{8/3}}\right]d\mathbf{r}\\ +2d\int_{\Omega_i}(\nabla\Delta_j\cdot\nabla\Delta_i)\left[-\frac{(\frac{9}{4})\nabla^2\Delta_i}{(\Delta_i+\bar{n})^{8/3}}\right.\\ \left.+\frac{(\frac{4}{3})(\nabla\Delta_i)^2}{(\Delta_i+\bar{n})^{11/3}}\right]d\mathbf{r}\ ,\end{aligned} \tag{4.21}$$

where terms in $\nabla^2\Delta_j$ have been collected together in the first integral along with those involving $\nabla\Delta_j$ in the second. The first integral may be transformed using Green's theorem into a volume integral and a surface integral. The volume integral is exactly that which is required in $-\Delta_j\circ V_i$. The surface integral contributes to the pair interaction for

$$2d\int_\Sigma\mathcal{F}[\Delta_i]\nabla\Delta_j\cdot d\mathbf{s}-2d\int_\Sigma\nabla\mathcal{F}[\Delta_i]\cdot d\mathbf{s}\Delta_j \tag{4.22}$$

on Σ, $\Delta_i=\Delta_j$, and $\nabla_n\Delta_j=-\nabla_n\Delta_i$, so that one gets immediately

$$2d\int_\Sigma-\nabla(\Delta_i\mathcal{F}[\Delta_i])\cdot d\mathbf{s} \tag{4.23}$$

or

$$2d\int_{R/2}^{\infty}-\frac{d}{dr}(\Delta\mathcal{F}[\Delta])2\pi r\,dr\frac{R}{2r} \tag{4.24}$$

$$=2\pi\,dR(\Delta\mathcal{F}[\Delta])_{r=R/2}\ . \tag{4.25}$$

In Eq. (4.25) we have used

$$\mathcal{F}[\Delta]=\frac{2\nabla^2\Delta}{(\Delta+\bar{n})^{5/3}}-\frac{\frac{9}{8}(\nabla\Delta)^2}{(\Delta+\bar{n})^{8/3}}\ . \tag{4.26}$$

Let us recall that the above derivation implies $\Delta_i=\Delta_j\ll\bar{n}$ on the Σ plane, though not everywhere. Let us now assume that the gradient of the density Δ may be measured in terms of a characteristic length l:

$$\nabla\Delta\sim\frac{\Delta}{l}\ . \tag{4.27}$$

One has for $\mathcal{F}[\Delta]$

$$\begin{aligned}\mathcal{F}[\Delta]&\sim\frac{2\Delta}{l^2(\Delta+\bar{n})^{5/3}}-\frac{\frac{9}{8}\Delta^2}{l^2(\Delta+\bar{n})^{8/3}}\\ &\sim\frac{\Delta}{l^2}\frac{2}{\bar{n}^{5/3}}\left[1-\frac{5}{3\bar{n}}-\frac{9}{8\bar{n}}\right]\ ,\end{aligned}$$

so that, if one works to lower order in $\Delta/\bar{n}$, one is left with

$$\mathcal{F}[\Delta]\sim\frac{2\nabla^2\Delta}{\bar{n}^{5/3}} \tag{4.28}$$

and Eq. (4.25) becomes

$$\frac{4\pi dR}{(\bar{n})^{5/3}}(\Delta\nabla^2\Delta)_{r=R/2}\ . \tag{4.29}$$

Let us return to the second integral in Eq. (4.22). It gives a surface contribution which is

$$2d\int_\Sigma\Delta_j\left[\frac{-\frac{9}{4}\nabla^2\Delta_i}{(\Delta_i+\bar{n})^{8/3}}+\frac{\frac{4}{3}(\nabla\Delta_i)^2}{(\Delta_i+\bar{n})^{11/3}}\right]\nabla\Delta_i\cdot d\mathbf{s}$$

which, according to Eq. (4.23), is of the form

$$2\pi\,dR\int_\Sigma\frac{-\frac{9}{4}\Delta^3}{(\bar{n})^{8/3}l^3}dr\ . \tag{4.30}$$

The integrand is of order $[1/(\bar{n})^{8/3}]\Delta^3/l^3$ to be compared with order $[1/(\bar{n})^{5/3}](\Delta^2/l^3)$ for the previous contribution in Eq. (4.25). Equation (4.30) is of higher order

in $\Delta/\bar{n}$ so that we can neglect it. Finally, the contribution of fourth-order gradients to the pair interaction is given by Eq. (4.29) only.

V. NUMERICAL RESULTS FOR THE GRADIENT EXPANSION PAIR INTERACTION IN LIQUID Na and Be

Let us first collect together the local TF plus gradient correction contributions to the pair potential. The result is

$$\phi_{\mathrm{TFG}}^{(2)}(R)=\tfrac{1}{4}R\left\{\left[V\left[\frac{R}{2}\right]\right]^2-\gamma^2\left[\Delta\left[\frac{R}{2}\right]\right]^2+\eta^2[\Delta\nabla^2\Delta]_{R/2}\right\}, \tag{5.1}$$

where η^2 is taken from Eq. (4.29).

We have performed the calculation of this pair potential for liquid Na and Be near freezing. Let us stress the fact that we always use in Eq. (5.1) the V and Δ provided by the DFT calculation,[9,11] never the potential and electron density which would result from the self-consistent solution of the TF+gradient correction problem.

A. Pair potential for liquid Na

Figure 3 has been constructed for Na. The curve labeled $\phi(R)$ is our electron theory pair potential for liquid Na near freezing. The curves labeled $\phi_{\mathrm{TFG}}^{(1)}$ and $\phi_{\mathrm{TFG}}^{(2)}$ add T_2 with $\lambda=\frac{1}{9}$ given by Kirznits[12] and T_2+T_4, respectively, to the curve labeled $\phi_{\mathrm{TF}}(R)$. These curves were calculated as follows: (i) $\phi_{\mathrm{TF}}(R)$ from Eq. (1.7), (ii) $\phi_{\mathrm{TFG}}^{(1)}(R)$ from Eq. (2.3), and $\phi_{\mathrm{TFG}}^{(2)}(R)$ from Eq. (5.1).

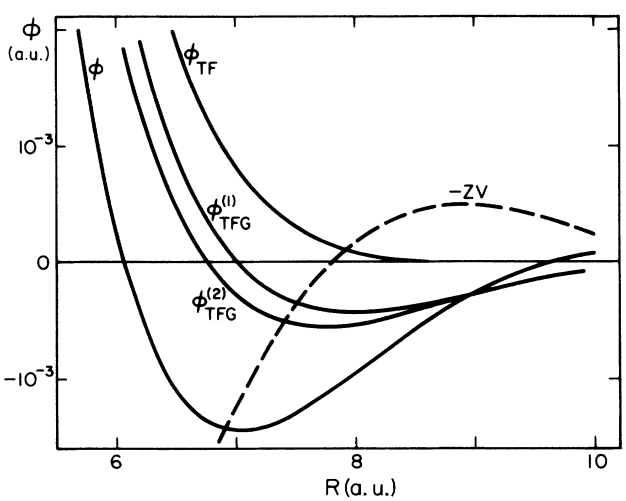

FIG. 3. This shows pair potentials calculated from local density (TF) theory plus density gradient corrections T_2 and T_4 to kinetic energy, for liquid Na near freezing. Various curves were obtained using $Q(R)$ in Fig. 1 from different degrees of approximation as follows. ϕ_{TF}, calculated from Eq. (1.7); $\phi_{\mathrm{TFG}}^{(1)}$ from Eq. (2.3) with $\lambda=\frac{1}{9}$ in which T_2 only is included; $\phi_{\mathrm{TFG}}^{(2)}$, from Eq. (5.1) containing both T_2 and T_4; $\phi_{\mathrm{LR}}=-ZV$; $\phi(R)$ is the pair potential obtained in our earlier work.

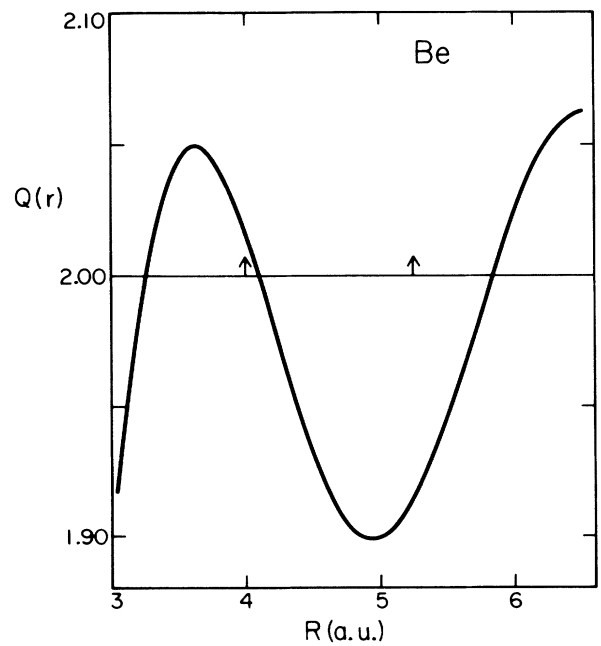

FIG. 4. Same as Fig. 1, but for liquid Be at a density equal to the solid density. Arrows denote first minimum and following maximum in "exact" pair potential $\phi(R)$.

B. Pair potential for liquid Be

It seemed of interest to perform similar calculations for the divalent liquid metal Be. First, the total valence screening charge $Q(R)$ was calculated using the DFT method.[11] It should be stressed that there are no adjust-

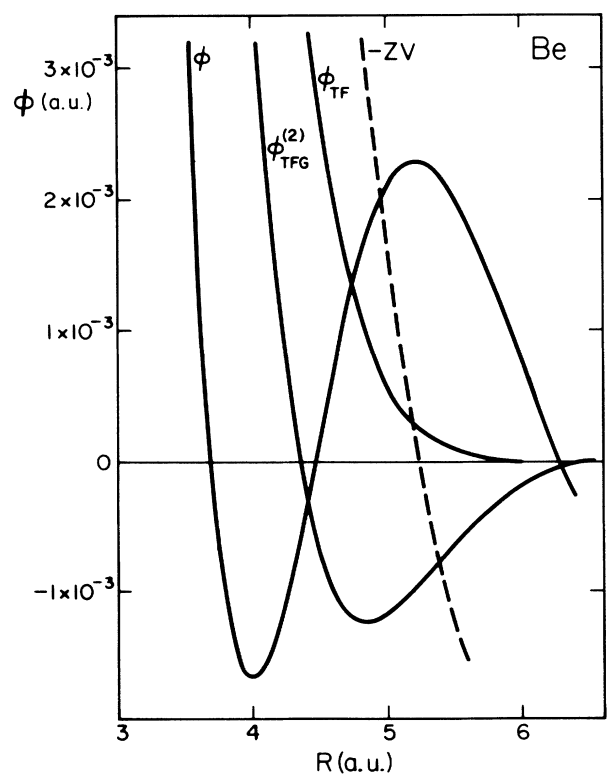

FIG. 5. Same as Fig. 3 but for Be.

able parameters in this calculation. The input into the full density functional calculation of $Q(R)$ is (a) the atomic number, (b) the mass density at freezing, and (c) an exchange-correlation potential.

Figure 4 shows $Q(R)$ versus R, which yields in linear response the pair interaction $\phi_{\rm LR}=-ZV$ in Fig. 5. This is shown compared with the "exact" $\phi(R)$ in the curve labeled ϕ. Again $\phi_{\rm TF}(R)$ and $\phi^{(2)}_{\rm TFG}$ have been constructed from $Q(R)$ in Fig. 4. The agreement for the well depth is quite comparable with that in liquid Na. The result is, at best, semiquantitative. However, it is more apparent for Be in Fig. 5 than for Na that the gradient expansion result is already a substantial improvement over the linear response curve $-ZV(R)$ around the principal minimum of $\phi(R)$.

These numerical results obviously indicate that the remaining nonlocality in the electronic kinetic energy is crucial to a quantitative calculation of the pair interaction in simple liquid metals. The discussion of these remaining contributions is the object of Sec. VI.

VI. REMAINING NONLOCALITY IN THE KINETIC ENERGY CONTRIBUTION TO THE PAIR INTERACTION

In the linear response approximation, the fully nonlocal kinetic energy change (plus exchange and correlation energy change) in bringing an ionic pair together from infinity, is given by (see Sec. IV A 1)

$$\begin{aligned}\Delta G(R)&=\tfrac{1}{2}G''[\bar{n}]\cdot[(\Delta_i+\Delta_j)^2-\Delta_i^2-\Delta_j^2]\\&=G''[\bar{n}]\cdot\Delta_i\cdot\Delta_j\\&=-\tfrac{1}{2}(V_i\cdot\Delta_j+V_j\cdot\Delta_i)\ .\end{aligned}\tag{6.1}$$

This expression may also be derived from the infinite order perturbation formalism of Stoddart and March,[13] which gives the changes in electron density and in kinetic energy density as

$$\Delta=n-\bar{n}=\sum_{p=1}^{\infty}n_p(r)\ ,\tag{6.2}$$

$$t-t_0=\mu\Delta-\sum_{p=1}^{\infty}\frac{p}{p+1}n_p(r)V(r)\ ,\tag{6.3}$$

with $V(r)$ the one-body potential in the Schrödinger equation. In this theory, exchange and correlation effects are neglected. The first-order term on the right-hand side of Eq. (6.3) does not contribute to the integrated kinetic energy. In linear response, the terms to be retained are only the $p=1$ terms, so that

$$\begin{aligned}\Delta T(R)&=-\tfrac{1}{2}(\Delta_i+\Delta_j)\cdot(V_i+V_j)+\tfrac{1}{2}\Delta_i\cdot V_i+\tfrac{1}{2}\Delta_j\cdot V_j\\&=-\tfrac{1}{2}(\Delta_i\cdot V_j+\Delta_j\cdot V_i)\ ,\end{aligned}$$

which is exactly Eq. (6.1) when exchange and correlation effects are neglected.

That Eq. (6.1) has achieved the summation of the gradient expansion of the kinetic energy terms in the pair interaction to all orders is now clear by rewriting the density-potential relation utilized in Eq. (1.5) as

$$V_1(\mathbf{r})=\int K(\mathbf{r}-s)\Delta_1(s)ds\tag{6.4}$$

with a similar expression for $V_2(\mathbf{r})$ in Eq. (6.1). Here K is a known kernel, given in Fourier transform by Stoddart and March[13] as

$$K(\mathbf{r}-\mathbf{s})=-(2\pi)^{-3}\int\frac{d\mathbf{q}\exp[i\mathbf{q}\cdot(\mathbf{r}-\mathbf{s})]}{J(q,k_f)}\ ,\tag{6.5}$$

where

$$J(q,k_f)=\frac{k_f}{\pi^2}\left[\frac{1}{2}+\frac{k_f}{2q}\left[1-\frac{q^2}{4k_f^2}\right]\ln\left|\frac{q+2k_f}{q-2k_f}\right|\right]\ .\tag{6.6}$$

By means of the small q expansion of $J(q,k_f)$, one gets

$$V_1(\mathbf{r})=-\frac{\pi^2}{k_f}[\Delta_1(\mathbf{r})-c_2\nabla_{\mathbf{r}}^2\Delta_1(\mathbf{r})+c_4\nabla_{\mathbf{r}}^2\nabla_{\mathbf{r}}^2\Delta_1(\mathbf{r})+\cdots]\ .\tag{6.7}$$

Substitution of this result (6.7) into Eq. (6.1), together with a similar equation for $V_2(\mathbf{r})$ in terms of $\Delta_2(\mathbf{r})$ gives back the early results of the linearized gradient expansion. Unfortunately, we are not able to achieve a similar resummation beyond the linear response approximation. To get a better feeling of the numerical importance of the terms beyond T_4, we can display the sum of the missing contribution as a function of R.

All the pair potentials plotted in Fig. 3 for liquid Na and Fig. 5 for liquid Be near freezing can be regarded as derivable from a single equation:

$$\phi(R)=\Delta G(R)-ZV(R)+\Delta U_1(R)\ .\tag{6.8}$$

Then the common element, for Na, for example, is the total potential-energy change

$$\Delta U(R)=-ZV(R)+\Delta U_1(R)\ ,\tag{6.9}$$

which is determined solely by the total valence screening charge $Q(R)$, plotted in Fig. 1 for Na and Fig. 4 for Be.

Thus, the kinetic plus exchange and correlation energy change $\Delta G(R)$ is solely responsible for the differences of the various curves for $\phi(R)$ in Figs. 3 and 5. We have now extracted the fully nonlocal energy change $\Delta G(R)$ from Eq. (6.8), using $\phi(R)$ and $-ZV(R)$ already plotted in Figs. 3 and 5, plus a calculation of $\Delta U_1(R)$ from

$$\Delta U_1(R)=\tfrac{1}{2}(\Delta_1\cdot V_2+\Delta_2\cdot V_1)\ ,\tag{6.10}$$

which is evidently the interaction potential energy between the displaced charge around one ionic center with the screened potential due to the other. The convolution involved in Eq. (6.10) is readily calculated in Fourier transform and the results are displayed for liquid Na and Be in Figs. 6 and 7, respectively. The difference between $\Delta T^{(2)}_{\rm TFG}(R)$ and $\Delta T(R)$ (equal to $\Delta G^{(2)}_{\rm TFG}-\Delta G$) is clearly the remaining nonlocality in the electronic kinetic-energy charge. Thus the difference $\Delta T(R)-\Delta T^{(2)}_{\rm TFG}(R)$ can be regarded as the effective sum of the remaining terms in the gradient expansion beyond T_2 and T_4.

The remaining question is whether what is embodied in

this difference is determined by the size and the shape of the total screening charge $Q(R)$ around the midpoint $R/2$ of the metallic bond.

VII. DISCUSSION AND SUMMARY

The main results of the present study are the low-order density-gradient equation (5.1) for the pair potential, and the calculation of the fully nonlocal electronic kinetic-energy charge $\Delta T(R)$ plotted in Figs. 6 and 7, for liquid Na and Be. The comparison of Eq. (5.1) with the pair potentials $\phi(R)$ including the fully nonlocal kinetic energy shows that Eq. (5.1) is not more than semiquantitative. However, its major merit is that it focuses on the importance of the form of the total valence screening charge $Q(R)$ around the midpoint of the metallic bond.

We think it possible that $\Delta T(R)-\Delta T^{(2)}_{\mathrm{TFG}}(R)$ may also be expressible, at least approximately, in terms of $Q(R/2)$ [or $V(R/2)$ or $\Delta(R/2)$]. Our argument is the following. The gradient expansion has dealt with the small-q components of the pair interaction, but cannot treat the components $q\sim 2k_F$. These components are responsible for the asymptotic behavior (Friedel oscillations):

$$\Delta(R)=\frac{A}{R^3}\cos(2k_F R)+O\left[\frac{1}{R^4}\right] \tag{7.1}$$

in linear response. In this asymptotic regime, the potential is

$$V(R)=\frac{\pi}{k_F^2}\Delta(R)+O\left[\frac{1}{R^4}\right] \tag{7.2}$$

so that it may be written as

$$V(R)=BR^3\left\{\left[\Delta\left[\frac{R}{2}\right]\right]^2-\frac{1}{4k_F^2}\left[\left.\frac{d\Delta}{dR}\right|_{R/2}\right]^{+2}\right\}, \tag{7.3}$$

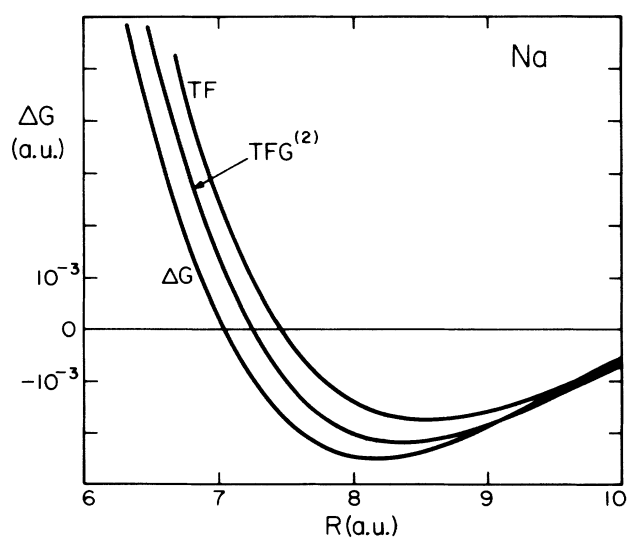

FIG. 6. This shows $\Delta G(R)$ for liquid Na, which is equivalent to total nonlocal kinetic-energy change $\Delta T(R)$ plus contribution from local exchange and correlation. The TF and fourth-order gradient contribution are also shown.

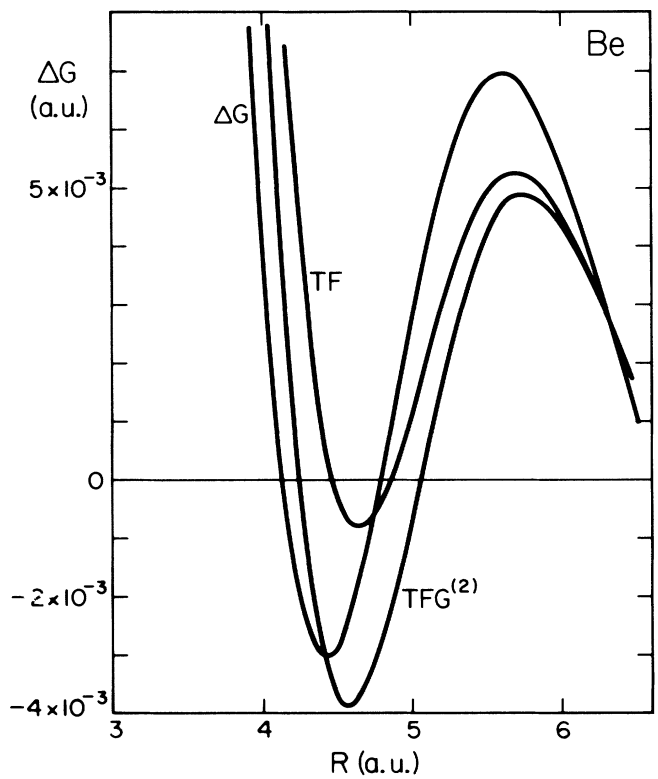

FIG. 7. Same as Fig. 6, but for Be.

suggesting that, here again, it may be expressed in terms of Δ at $R/2$. It is not obvious whether this argument holds beyond the linear approximation, when a phase shift has to be introduced into Eq. (7.1). Clearly, further work is called for before a definitive conclusion can be reached on this point. A convenient approach could be the use of the formulation of ϕ in terms of the pressure tensor in the symmetry plane of the "molecule," as proposed by More.[14]

The final remarks concern the potential interest of the present study for the theory of bonding in free space molecules. Though, of course, a different derivation must be found (due to the lack of uniform background density $\bar{n}$), some of the present ideas should be relevant. In the case of "molecules" in high-temperature plasmas, where Friedel oscillations are damped by temperature effects, the TF and low-order gradient expansion results should become increasingly quantitative.

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APPENDIX: VON WEIZSÄCKER'S GENERALIZATION OF TF THEORY IN LINEAR RESPONSE FOR ARBITRARY λ IN Eq. (2.1)

The purpose of this appendix is to effect the general demonstration of Eq. (2.3) with arbitrary value of λ in the first gradient correction to the *TF* kinetic energy. The value $\lambda=1$ corresponds to the original choice of von Weizsäcker.[7] The later work of Kirznits[12] and subsequently of Jones and Young[15] showed that the consistent generalization of TF theory for its range of validity of potentials which vary by but a small fraction of themselves over a characteristic de Broglie wavelength of the system yielded the value $\lambda=\frac{1}{9}$, used in constructing Figs. 3 and 5.

Taking the results of Jones and Young[15] as a convenient starting point, the screened ionic potential V in linear response theory can be written in Fourier transform for a general value of λ as

$$(2\pi)^3 V(r)=-4\pi Z\int e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{q}\frac{1}{q^2+4\pi\dfrac{k_F}{\pi^2}\dfrac{1}{1+\dfrac{3\lambda}{4k_F^2}q^2}}$$

$$=-4\pi Z\int e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{q}\frac{1+\alpha^2q^2}{\alpha^2q^4+q^2+q_{\mathrm{TF}}^2}\ , \qquad \text{(A1)}$$

where

$$\alpha^2=\frac{3\lambda}{4k_F^2}\ . \qquad \text{(A2)}$$

The set of the denominator $\alpha^2q^4+q^2+q_{\mathrm{TF}}^2$ may be conveniently classified by the parameter

$$\Delta=1-4\alpha^2q_{\mathrm{TF}}^2\ , \qquad \text{(A3)}$$

where Δ, being independent of position, is not to be confused with the displaced charge $\Delta(r)$.

1. $\Delta>0$

The roots are $(-1-\sqrt{\Delta})/2\alpha^2$ and $(-1+\sqrt{\Delta})/2\alpha^2$ real, negative. Let us define

$$q_0^2=\frac{1+\sqrt{\Delta}}{2\alpha^2},\quad q_1^2=\frac{1-\sqrt{\Delta}}{2\alpha^2}\ . \qquad \text{(A4)}$$

After a straightforward decomposition of the integrand in Eq. (A1), one obtains the screened ionic potential V in the form

$$V(r)=-\frac{Z}{r}\frac{1}{2}\left[\frac{(\sqrt{\Delta}-1)}{\sqrt{\Delta}}e^{-q_0r}+\frac{(\sqrt{\Delta}+1)}{\sqrt{\Delta}}e^{-q_1r}\right]. \qquad \text{(A5)}$$

From Poisson's equation, one finds the displaced charge Δ as

$$\Delta(r)=\frac{1}{4\pi r}\left[+\frac{Z}{2\sqrt{\Delta}}\right][(\sqrt{\Delta}-1)q_0^2e^{-q_0r}+(\sqrt{\Delta}+1)q_1^2e^{-q_1r}]\ . \qquad \text{(A6)}$$

Using Eq. (A5) one obtains

$$\frac{r}{4}\left[V\left[\frac{r}{2}\right]\right]^2=\frac{Z^2}{4\Delta r}\left[(\sqrt{\Delta}-1)^2e^{-q_0r}+(\sqrt{\Delta+1})^2e^{-q_1r}+2(\Delta-1)e^{-(q_0+q_1)(r/2)}\right]. \qquad \text{(A7)}$$

Thus it follows that

$$-ZV(r)-\frac{r}{4}\left[V\left[\frac{r}{2}\right]\right]^2=-\frac{Z^2}{r}\frac{\alpha^4q_0^2q_1^2}{\Delta}(e^{-q_1r}+e^{-q_0r}-2e^{-(q_0+q_1)(r/2)})\ . \qquad \text{(A8)}$$

Similarly the nonlocal contribution to ϕ is directly related to

$$4\pi r\left[\Delta\left[\frac{r}{2}\right]\right]^2=\frac{Z^2}{\pi\Delta r}q_{\mathrm{TF}}^4(e^{-q_0r}+e^{-q_1r}-2e^{-(q_0+q_1)(r/2)})\ . \qquad \text{(A9)}$$

Hence it follows that

$$-ZV(r)-\frac{r}{4}\left[V\left[\frac{r}{2}\right]\right]^2=-\frac{\pi\alpha^2}{q_{\mathrm{TF}}^2}4\pi r\left[\Delta\left[\frac{r}{2}\right]\right]^2, \qquad \text{(A10)}$$

where

$$\frac{4\pi^2\alpha^2}{q_{\mathrm{TF}}^2}=\frac{\pi\lambda}{4\bar{n}}\ , \qquad \text{(A11)}$$

which agrees with Eq. (2.3) in linear response theory.

2. $\Delta<0$

Here $\Delta=1-4\alpha^2q_{\mathrm{TF}}^2<0$ and the roots are $(-1-i\sqrt{|\Delta|})/2\alpha^2$ and $(-1+i\sqrt{|\Delta|})/2\alpha^2$, with the real part negative. Let us define

$$q_a^2=\frac{1+i\sqrt{|\Delta|}}{2\alpha^2},\quad (q_a^*)^2=\frac{1-i\sqrt{|\Delta|}}{2\alpha^2}\ , \qquad \text{(A12)}$$

and retain for q_a and q_a^* the solutions with positive real part.

Hence the screened potential is now

$$V(r)=-\frac{Z}{r}\frac{1}{2}\left[\frac{i\sqrt{|\Delta|}-1}{i\sqrt{|\Delta|}}e^{-q_ar}+\frac{i\sqrt{|\Delta|}+1}{i\sqrt{|\Delta|}}e^{-q_a^*r}\right], \qquad \text{(A13)}$$

where

$$q_a^2=\rho^2 e^{i\theta},\quad \rho^2=\frac{\sqrt{1+|\Delta|}}{2\alpha^2}=\frac{q_{\rm TF}}{\alpha} \tag{A14}$$

with

$$\tan\theta=\sqrt{|\Delta|},\quad 0\le\theta\le\frac{\pi}{2}\ .$$

Thus

$$q_a=\rho e^{i(\theta/2)}\ ,$$
$$q_a^*=\rho e^{-i(\theta/2)}\ .$$

The potential becomes

$$V(r)=-\frac{Z}{2r}e^{-\rho\cos(\theta/2)r}\left[2\cos\left[\rho\sin\frac{\theta}{2}r\right]-\frac{i}{\sqrt{|\Delta|}}2i\sin\left[\rho\sin\frac{\theta}{2}r\right]\right]\ . \tag{A15}$$

Writing

$$\rho\cos\frac{\theta}{2}=\mu,\quad \rho\sin\frac{\theta}{2}=\nu$$

one finds

$$V(r)=-\frac{Z}{r}e^{-\mu r}\left[\cos\nu r+\frac{1}{\sqrt{|\Delta|}}\sin\nu r\right]\ . \tag{A16}$$

Using Poisson's equation with V in the form

$$V(r)=-\frac{Z}{r}\frac{1}{\sin\theta}\sin(\nu r+\theta)e^{-\mu r} \tag{A17}$$

yields the displaced charge $\Delta(r)$ as

$$\Delta(r)=\frac{Z}{r}\frac{1}{\sin\theta}\left[\frac{1}{4\pi}\frac{q_{\rm TF}}{\alpha}\right]\sin\nu r e^{-\mu r}\ . \tag{A18}$$

Hence

$$\frac{r}{4}\left[V\left[\frac{r}{2}\right]\right]^2=\frac{Z^2}{r}\frac{1}{\sin^2\theta}\sin^2\left[\frac{\nu r}{2}+\theta\right]e^{-\mu r}\ . \tag{A19}$$

It follows that

$$-ZV(r)-\frac{r}{4}\left[V\left[\frac{r}{2}\right]\right]^2=\frac{Z^2}{r}\frac{1}{\sin^2\theta}e^{-\mu r}\left[\sin\theta\sin(\nu r+\theta)-\sin^2\left[\frac{\nu r}{2}+\theta\right]\right] \tag{A20}$$

and

$$r\left[\Delta\left[\frac{r}{2}\right]\right]^2=\frac{Z^2}{r}\frac{1}{4\pi^2}\frac{q_{\rm TF}^2}{\alpha^2}\frac{1}{\sin^2\theta}\sin^2\left[\frac{\nu r}{2}\right]e^{-\mu r}\ . \tag{A21}$$

The transformation

$$\sin\theta\sin(\nu r+\theta)-\sin^2\left[\frac{\nu r}{2}+\theta\right]=-\sin^2\frac{\nu r}{2} \tag{A22}$$

then yields

$$-ZV(r)-\frac{r}{4}\left[V\left[\frac{r}{2}\right]\right]^2=-\frac{Z^2}{r}\frac{1}{\sin^2\theta}e^{-\mu r}\sin^2\frac{\nu r}{2} \tag{A23}$$

and comparison of Eqs. (A21) and (A23) leads to

$$-ZV(r)-\frac{r}{4}\left[V\left[\frac{r}{2}\right]\right]^2=-\frac{2\pi}{\bar n}\frac{\lambda}{8}r\left[\Delta\left[\frac{r}{2}\right]\right]^2\ . \tag{A24}$$

This is again equivalent to Eq. (2.3) in the linear response regime.

Hence the conclusion is that both for $\Delta>0$ and $\Delta<0$ in Eq. (A13), the result in linear response for the pair potential $\phi(r)$ is

$$\phi(r)=-ZV(r)=\frac{r}{4}\left[V\left[\frac{r}{2}\right]\right]^2-\frac{\pi\lambda}{4\bar n}r\left[\Delta\left[\frac{r}{2}\right]\right]^2\ . \tag{A25}$$

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