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# Charge densities and interionic potentials in simple metals: Nonlinear effects. I

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Starting from the Hohenberg-Kohn-Sham equations, expressions are derived for the linear-response charge density induced by a nonlocal pseudopotential embedded in an electron gas and for the corresponding interionic pair potential. It is emphasized that an accurate calculation of the charge density is an essential prerequisite for the generation of a reliable potential. This point is illustrated by making a comparison with Dagens's self-consistent calculations of the charge density induced by an isolated $Na^+$ ion. It is shown that nonlinear effects in both the density and the potential cannot be ignored. However by adjusting the pseudopotential parameters to fit the self-consistent charge density and thus simulate the nonlinear terms, a reliable and useful interionic potential is generated. Thus the essential simplicity of the pseudopotential perturbation approach to the theory of metals can be retained and nonlinear effects can be incorporated into it in a straightforward manner.

## I. INTRODUCTION

In this work we wish to examine the problem of constructing reliable interionic pair potentials to be used in the study of disordered simple metals, i.e., liquids, defect systems, disordered alloys, etc. By simple metals we mean those for which the ionic core electrons are tightly bound, giving rise to no significant overlap with nearest neighbors, e.g., Al, Na, etc. This problem is usually handled by examining the cohesive energy of the system. The full ionic potential is replaced by a pseudopotential and the cohesive energy is expanded in a perturbation series to second order in the pseudopotential. Conduction-electron exchange and correlation effects are accounted for by use of a dielectric function. The second-order term can then be written as the sum of overlapping interionic pair potentials centered on each ion site. Now it is highly desirable to terminate the perturbation expansion at this point since the treatment of the disordered system becomes virtually intractable if higher-order terms are included (see, e.g., Wiser and Greenfield[1]). This of course requires that the conduction-electron charge density be a *linear* function of the external potential, an approximation which is by no means completely justified and which is investigated in this paper.

Before proceeding any further let us emphasize one important point. If we know the charge density as a function of position in a disordered system, then Hohenberg-Kohn-Sham (HKS) theory[2-4] tells us that we can, at least in principle, calculate the cohesive energy; i.e., the charge density plays a central role in the problem, a fact which we feel should be and can be exploited to great advantage when calculating pair potentials. Of course without any definite knowledge of the charge density we are no further ahead, but the calculations of Dagens[5] for Na and Li provide just the information that is needed. Briefly, Dagens calculated the charge density induced by a full ionic potential embedded in an electron gas using the HKS self-consistent equations. The calculation is precisely equivalent to summing the corresponding pseudopotential perturbation approach to all orders (neglecting core effects).

Let us now outline the procedure described in the following sections of this paper. First the full ionic potential for the metal in question is converted to a pseudopotential. In general this gives rise to a nonlocal pseudopotential (e.g., see Rasolt and Taylor[6]). In Sec. II A using the HKS equations we derive an expression for the linear-response charge density induced by a nonlocal pseudopotential placed in an electron gas with exchange and relation effects included. Although this expression is much more complicated to evaluate numerically than for a local pseudopotential, it is by no means intractable. Numerical procedures are given in Sec. III. The calculated linear-response charge density with nonlocal effects included can then be compared with Dagens' self-consistent calculations. In every system considered so far we have found significant differences between the two calculations indicating that nonlinear effects can be quite important. To include the nonlinear terms in the calculation we simply adjust the pseudopotential parameters so as to reproduce accurately the self-consistent charge density for $r$ values outside the ionic core region. With these pseudopotentials we assume that we can then extend the calculation of the charge densities further, to a random array of ions. The corresponding interionic pair potentials are then derived in Secs II B and II C. By this procedure we have thus corrected for nonlinear effects and yet maintained the simplicity of writing the cohesive energy as a sum of pair potentials.

In Sec. IV using Na as an example we calculate the isolated ion charge density, the phonon dispersion curves, and the pair potential. Without any correction for nonlinear effects the phonon dispersion curves differ from experiment by about 5% to 10%, these errors being almost entirely removed by invoking the above procedure. Concluding remarks are given in Sec. V. Calculations have been performed on other simple metals giving similar results and these will be reported in a later publication.

## II. BASIC FORMULATION

### A. Charge distribution around an isolated ion embedded in a homogeneous electron gas

The charge density induced by an isolated ion embedded in an electron gas can be calculated in several ways. A particularly interesting method is the solution of the HKS equations in the presence of the full ionic potential. This method is in principle exact if the precise form of the exchange and correlation potential $[v_{\mathrm{xc}}(r) = \delta E_{\mathrm{xc}}(n)/\delta n]$ is known. But even given the knowledge of $v_{\mathrm{xc}}$, the procedure is quite difficult and, most importantly, cannot be applied to a random array of ions.

An alternative approach is to convert the full ionic potential to a formally equivalent pseudopotential and use perturbation theory to solve for the charge density. By a formally equivalent pseudopotential we mean one which reproduces, exactly, the phase shifts of the full potential in the region of interest. Such a pseudopotential can be constructed, for example, by using the variable phase method.[6,8] Not surprisingly, it turns out that in many materials nonlocal effects are quite important and a simple local theory of the charge density is inadequate. Hence in this section we describe the derivation of the charge density induced by a nonlocal pseudopotential. We shall restrict ourselves to energy-independent pseudopotentials and we shall retain only the first-order term (the linear-response term), using the pseudopotential as an ordering parameter, in the perturbation expansion. This latter approximation is consistent with the conventional use of pseudopotential theory, the validity of which will be discussed later.

We start with the HKS equation

$$(\hat{T} + \hat{V})\,|\phi_{\vec{k}}\rangle = E_{\vec{k}}\,|\phi_{\vec{k}}\rangle \ . \tag{1}$$

(Note that the $|\phi_{\vec{k}}\rangle$ are *not* single particle states), where in $\vec{r}$ space

$$\langle \vec{r}\,|\hat{T}|\,\vec{r}\,'\rangle = -(\hbar^2/2m)\nabla^2 \ , \tag{2}$$

$$\langle \vec{r}\,|\hat{V}|\,\vec{r}\,'\rangle = v_p(\vec{r}, \vec{r}\,') + \left(e^2 \int \frac{n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}\, d\vec{r}\,' + v_{\mathrm{xc}}(n)\right)\delta(\vec{r} - \vec{r}\,') \tag{3}$$

and $v_p(\vec{r}, \vec{r}\,')$ is the nonlocal pseudopotential formally equivalent to the ionic potential. The induced pseudodensity is given by

$$\begin{aligned} n(\vec{r}) &= \sum_{\vec{k}} \langle \phi_{\vec{k}}\,|\vec{r}\rangle\langle\vec{r}\,|\,\phi_{\vec{k}}\rangle\Theta^{<}(\vec{k}) \\ &= \sum_{\vec{k}} \phi^{*}_{\vec{k}}(\vec{r})\phi_{\vec{k}}(\vec{r})\Theta^{<}(\vec{k}) \ , \end{aligned} \tag{4}$$

where $\Theta^{<}(\vec{k})$ is 1 for $k \leqslant k_F$ and 0 otherwise.

Before we proceed any further we should make two comments about the validity of Eq. (3). First let us note that the use of the variable-phase method enables us to construct $v_p(\vec{r}, \vec{r}\,')$ by a direct transformation from a full *local* ionic potential. Thus there is no inconsistency in applying the HKS scheme to such a nonlocal pseudopotential. If the ionic potential were nonlocal, then the whole concept of energy being a functional of the density would break down. Secondly, let us note that a variable phase pseudopotential consists, for each angular momentum $l$ value, of a square well of constant depth $A_l$ for $r < R_l$ and for $r > R_l$ it is precisely the ionic potential. Now if the electron potential [i.e., the last two terms of Eq. (3)] were constant for $r < R_L$ (the largest $R_l$), the pseudodensity obtained by solving Eqs. (1)–(4) would be identical to the full ionic density for $r > R_L$. Since the electron potential is slowly varying for small $r$, it is desirable to choose $R_L$ to be as small as possible in order to enhance the validity of Eq. (3) as well as to enlarge the region for which $n(r)$ is meaningful. On the other hand, it must be remembered that the smaller is $R_L$, the larger is the magnitude of the pseudopotential and thus the less valid is linear response.

To solve Eqs. (1)–(4) for the density to linear order in $\hat{V}$ (or equivalently to linear order in $\hat{v}_p$) is not difficult. $|\phi_{\vec{k}}\rangle$ can be written

$$|\phi_{\vec{k}}\rangle = |\vec{k}\rangle + \sum_{\vec{q}} G^{\vec{k}}_{\vec{k}+\vec{q}}\,|\vec{k}+\vec{q}\rangle \ , \tag{5}$$

where $\langle\vec{r}\,|\vec{k}\rangle = \Omega^{-1/2}e^{i\vec{k}\cdot\vec{r}}$, $\Omega$ is the volume of the system

$$G^{\vec{k}}_{\vec{k}+\vec{q}} = \frac{\langle\vec{k}+\vec{q}\,|\,\hat{V}\,|\vec{k}\rangle}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}}} \tag{6}$$

and

$$\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m} \ .$$

From Eqs. (4) and (5) we obtain to linear order in $\hat{V}$

$$\delta n(\vec{q}) = \int \delta n(\vec{r})e^{-i\vec{q}\cdot\vec{r}}\, d\vec{r}$$

$$=2\sum_{\vec{k}}\left(G^{\vec{k}*}_{\vec{k}-\vec{q}}+G^{\vec{k}}_{\vec{k}+\vec{q}}\right)\Theta^{<}(\vec{k})\ , \tag{7}$$

where $\delta n(\vec{r})=n(\vec{r})-n_0$ and $n_0$ is the density of the uniform electron gas. Now by expanding $v_{\text{xc}}(n)$ to linear order in $\delta n(\vec{r})$, i.e., by writing

$$v_{\text{xc}}(n)=F(n_0)+\int F'(n_0,\vec{r}-\vec{r}\,')\delta n(\vec{r}\,')\,d\vec{r}\,'\ ,$$

we can combine Eqs. (3) and (6) to obtain

$$G^{\vec{k}}_{\vec{k}+\vec{q}}=\frac{\langle\vec{k}+\vec{q}\,|\,\hat{v}_p\,|\vec{k}\rangle}{\epsilon_{\vec{k}}-\epsilon_{\vec{k}+\vec{q}}}+\frac{[4\pi e^2/q^2+F'(n_0,q)]\delta n(q)}{\Omega(\epsilon_{\vec{k}}-\epsilon_{\vec{k}+\vec{q}}}\ , \tag{8}$$

where (e.g., see Geldart *et al.*[9])

$$F'(n_0,q)=\frac{1}{\Pi(q)}-\frac{1}{\Pi_0(q)}\ . \tag{9}$$

$\Pi(q)$ is the electron-gas screening function related to the dielectric function by

$$\epsilon(q)=1+\frac{4\pi e^2}{q^2}\Pi(q)\ .$$

$\Pi_0(q)$ is the corresponding function for the noninteracting electron gas. Combining Eqs. (7)–(9) we find that

$$\delta n(q)=-H_1(q)\chi(q)/\Pi_0(q)\ , \tag{10}$$

where

$$H_1(q)=-4\sum_{\vec{k}}\frac{\langle\vec{k}+\vec{q}\,|\,\hat{v}_p\,|\vec{k}\rangle}{\epsilon_{\vec{k}}-\epsilon_{\vec{k}+\vec{q}}}\Theta^{<}(\vec{k}) \tag{11}$$

and

$$\chi(q)=\frac{\Pi(q)}{1+(4\pi e^2/q^2)\Pi(q)}\ . \tag{12}$$

For completeness we note that

$$\Pi_0(q)=-\frac{4}{\Omega}\sum_{\vec{k}}\frac{\Theta^{<}(\vec{k})}{\epsilon_{\vec{k}}-\epsilon_{\vec{k}+\vec{q}}}=\frac{mk_F}{\pi^2\hbar^2}\left(\frac{1}{2}+\frac{4k_F^2-q^2}{8k_Fq}\ln\left|\frac{q+2k_F}{q-2k_F}\right|\right). \tag{13}$$

### B. Cohesive energy of an arbitrary array of ions embedded in a homogeneous electron gas

For an arbitrary array of ions Eq. (1) becomes

$$(\hat{T}+\hat{V}_T)\,|\,\phi_{\vec{k}}\rangle=E_{\vec{k}}\,|\,\phi_{\vec{k}}\rangle\ , \tag{14}$$

with the density given by Eq. (4):

$$\langle\vec{r}\,|\,\hat{V}_T\,|\vec{r}\,'\rangle=\sum_m v_p(\vec{r}-\vec{R}_m,\vec{r}\,'-\vec{R}_m)+\left(e^2\int\frac{n(\vec{r}\,'')}{|\vec{r}-\vec{r}\,''|}d\vec{r}\,''+v_{\text{xc}}(n)\right)\delta(\vec{r}-\vec{r}\,')\ , \tag{15}$$

where the positions of the ions are denoted by $\vec{R}_m$. The energy of the system can be written as

$$E(n)=\sum_{\vec{k}}E_{\vec{k}}\Theta^{<}(\vec{k})-\frac{e^2}{2}\iint\frac{\delta n(\vec{r}\,')\delta n(\vec{r})}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,d\vec{r}\,'-\int v_{\text{xc}}(\vec{r})\delta n(\vec{r})d\vec{r}+E_{\text{xc}}(n)+\tfrac{1}{2}(Ze)^2\sum_{m\neq m'}\frac{1}{|\vec{R}_m-\vec{R}_{m'}|}\ . \tag{16}$$

The last term is the bare Coulomb interaction between the ions of charge $Ze$. The second and third terms have to be subtracted because the electron-electron energy has been counted twice in the first term. Strictly speaking, Eq. (16) should be evaluated using the full ionic density for $\delta n(\vec{r})$. However, we assert that no significant error is incurred by using the pseudodensity generated by replacing the ionic potential by a pseudopotential. That this is satisfactory for simple metals [specifically the part depending on the structure of the random system; see Eq. (24) below] is strongly suggested by the works of Pick and Sarma[10] and Vosko.[11] We expand $E_{\vec{k}}$ to second order in $\hat{V}_T$, i.e.,

$$E_{\vec{k}}=\epsilon_{\vec{k}}+\langle\vec{k}\,|\,\hat{V}_T\,|\vec{k}\rangle+\sum_{\vec{q}}\frac{|\langle\vec{k}\,|\,\hat{V}_T\,|\vec{k}+\vec{q}\rangle|^2}{\epsilon_{\vec{k}}-\epsilon_{\vec{k}+\vec{q}}}\ . \tag{17}$$

This of course is consistent with calculating $\delta n(\vec{r})$ to first order in $\hat{V}_T$. We note that

$$\langle\vec{k}+\vec{q}\,|\,\hat{V}_T\,|\vec{k}\rangle=\langle\vec{k}+\vec{q}\,|\,\hat{V}\,|\vec{k}\rangle S(q)\ , \tag{18}$$

where, using Eqs. (6) and (8)–(11),

$$\langle\vec{k}+\vec{q}\,|\,\hat{V}\,|\vec{k}\rangle=\langle\vec{k}+\vec{q}\,|\,\hat{v}_p\,|\vec{k}\rangle-\frac{H_1(q)}{\Omega}\left(\frac{\Pi(q)-\chi(q)}{\Pi_0^2(q)}\right)\ . \tag{19}$$

In this case

$$\delta n(q)=-H_1(q)[\chi(q)/\Pi_0(q)]S(q)\ . \tag{20}$$

$S(\vec{q})=\sum_m e^{-i\vec{q}\cdot\vec{R}_m}$ is the usual geometric structure factor. Using Eqs. (17)–(19) and neglecting terms independent of the relative positions of the ions we get

$$\sum_{\vec{k}}E_{\vec{k}}\Theta^{<}(\vec{k})=-\sum_q\left[H_2(q)+\frac{H_1^2(q)}{\Omega\Pi_0(q)}\left(\frac{\chi^2(q)}{\Pi_0^2(q)}-1\right)\right]|S(q)|^2\ , \tag{21}$$

where

$$H_2(q)=-4\sum_{\vec{k}}\frac{|\langle\vec{k}+\vec{q}\,|\,\hat{v}_p\,|\vec{k}\rangle|^2}{\epsilon_{\vec{k}}-\epsilon_{\vec{k}+\vec{q}}}\Theta^{<}(\vec{k})\ . \tag{22}$$

The electron-electron energy $E_{\text{el}}$ which is minus the second and third terms of Eq. (16) can be written

$$E_{\text{el}}=\frac{1}{2\Omega}\sum_q\left(\frac{4\pi e^2}{q^2}+F'(n_0,q)\right)\delta n^2(q)\ . \tag{23}$$

Inserting Eqs. (9) and (20) into (23) and then inserting the resulting expression along with Eq. (21) into Eq. (16) we find that

$$E(n)=E_0+\frac{1}{2}\sum_{m,m'}V_{\mathrm{II}}(|\vec{R}_m-\vec{R}_{m'}|)\ , \tag{24}$$

where $E_0$ is independent of the relative position of the ions. The interionic potential $V_{\mathrm{II}}(r)$ is given by

$$V_{\mathrm{II}}(r)=\frac{(Ze)^2}{r}-\frac{(Ze)^2}{2\pi^2}\int\frac{F(q)}{q^2}e^{-i\vec{q}\cdot\vec{r}}\,d\vec{q} \tag{25}$$

and the energy–wave-number characteristic $F(q)$ is given by

$$F(q)=\frac{\Omega q^2}{4\pi(Ze)^2}\left[H_2(q)-\frac{H_1^2(q)}{\Omega\Pi_0(q)}\left(1-\frac{\chi(q)}{\Pi_0(q)}\right)\right]\ . \tag{26}$$

The functions $H_1(q)$, $H_2(q)$, and $\chi(q)$ are defined by Eqs. (11), (22), and (12), respectively. All of the exchange and correlation effects are contained in $\chi(q)$, and it is only necessary to choose an appropriate $\Pi(q)$ to take these into account.

### C. The cohesive energy of a two-component system

Finally we note that the energy of a two-component system with components $\alpha$ and $\beta$ can easily be written down using the same techniques as in the previous Sec. II A. Starting from the appropriate equation equivalent to Eq. (16) and noting that in this case

$$\langle\vec{k}+\vec{q}\,|\,\hat{V}_T\,|\vec{k}\rangle=\langle\vec{k}+\vec{q}\,|\,\hat{V}^{\alpha}\,|\vec{k}\rangle S^{\alpha}(q)+\langle\vec{k}+\vec{q}\,|\,\hat{V}^{\beta}\,|\vec{k}\rangle S^{\beta}(q)\ , \tag{27}$$

it is straightforward to derive the result

$$E^{\alpha\beta}(n)=E_0^{\alpha\beta}+\frac{1}{2}\sum_{n\neq n'}V_{\mathrm{II}}^{\alpha\alpha}(|\vec{R}_n^{\alpha}-\vec{R}_{n'}^{\alpha}|)+\frac{1}{2}\sum_{m\neq m'}V_{\mathrm{II}}^{\beta\beta}$$

$$\times(|\vec{R}_m^{\beta}-\vec{R}_{m'}^{\beta}|)+\sum_{n,m}V_{\mathrm{II}}^{\alpha\beta}(|\vec{R}_n^{\alpha}-\vec{R}_m^{\beta}|). \tag{28}$$

$V_{\mathrm{II}}^{\alpha\alpha}$ and $V_{\mathrm{II}}^{\beta\beta}$ have identical form to Eq. (25) with $\hat{v}_p$ replaced by $\hat{v}_p^{\alpha}(\hat{v}_p^{\beta})$ and $Z$ replaced by $Z^{\alpha}$ $(Z^{\beta})$. $V_{\mathrm{II}}^{\alpha\beta}$ takes the form

$$V_{\mathrm{II}}^{\alpha\beta}(r)=\frac{Z^{\alpha}Z^{\beta}e^2}{r}-\frac{Z^{\alpha}Z^{\beta}e^2}{2\pi^2}\int\frac{F^{\alpha\beta}(q)}{q^2}e^{-i\vec{q}\cdot\vec{r}}\,d\vec{q}\ , \tag{29}$$

where

$$F^{\alpha\beta}(q)=\frac{\Omega q^2}{4\pi Z^{\alpha}Z^{\beta}e^2}\left[H_2^{\alpha\beta}(q)-\frac{H_1^{\alpha}(q)H_1^{\beta}(q)}{\Omega\Pi_0(q)}\left(1-\frac{\chi(q)}{\Pi_0(q)}\right)\right], \tag{30}$$

$$H_2^{\alpha\beta}(q)=-4\sum_k\frac{\langle\vec{k}+\vec{q}\,|\,\hat{v}_p^{\alpha}\,|k\rangle\langle k\,|\,\hat{v}_p^{\beta}\,|\vec{k}+\vec{q}\rangle}{\epsilon_{\vec{k}}-\epsilon_{\vec{k}+\vec{q}}}\ , \tag{31}$$

and $H_1^{\alpha}(q)$, $H_1^{\beta}(q)$ are given by Eq. (11) with $\hat{v}_p$ replaced by $\hat{v}_p^{\alpha}(\hat{v}_p^{\beta})$. In Eqs. (29)–(31) we have all the information necessary to calculate the interionic potentials for an alloy system. A particularly interesting case is that of the isolated impurity diffusing through a host lattice which can be treated using a potential derived from Eqs. (29)–(31).

## III. REDUCTION TO A FORM SUITABLE FOR NUMERICAL COMPUTATION

One of the major difficulties encountered when using formulas such as those derived in Sec. II, is the evaluation of sums or integrals of the form appearing in Eq. (11). In this section we use a technique employed by Geldart and Taylor[12] to reduce these integrals to a relatively simple form. We then rewrite Eqs. (10), (26), (30) in terms of the simplified integrals.

First we note that

$$\langle\vec{r}\,|\,\hat{v}_p\,|\vec{r}\,'\rangle=v_p(\vec{r},\vec{r}\,')=v_p(\hat{R}\vec{r},\hat{R}\vec{r}\,')=v_p(\vec{r}\,',\vec{r})\ ,$$

the last relation being a consequence of specializing $\hat{v}_p$ to being real and Hermitian ($\hat{R}\equiv$ rotation plus inversion). Keeping in mind these properties of $\hat{v}_p$ we take the following approach. We rewrite $H_1(q)$ [Eq. (11)] in integral form

$$H_1(q)=\frac{4\Omega}{(2\pi)^3}\frac{2m}{\hbar^2}\int\frac{\langle\vec{k}+\vec{q}\,|\,\hat{v}_p\,|\vec{k}\rangle}{(\vec{k}+\vec{q})^2-k^2}\,d\vec{k}\,\Theta^{<}(\vec{k})\Theta^{>}(\vec{k}+\vec{q})\ ,$$

where $\Theta^{>}(\vec{k})=1-\Theta^{<}(\vec{k})$. By symmetry all contributions to $H_1(q)$ for $|\vec{k}+\vec{q}|>k_F$ sum to zero so that the introduction of $\Theta^{>}(\vec{k}+\vec{q})$ is a matter of convenience. Now the pseudopotential $\hat{v}_p$ can be split into a local part and a nonlocal part. We can therefore write

$$\langle\vec{k}+\vec{q}\,|\,\hat{v}_p\,|\vec{k}\rangle=\frac{4\pi Ze^2}{\Omega q^2}[M_{\mathrm{L}}(q)+M_{\mathrm{NL}}(\vec{k}+\vec{q},\vec{k})] \tag{32}$$

and

$$H_1(q)=\frac{4\pi Ze^2}{q^2}\Pi_0(q)M_{\mathrm{L}}(q)+\frac{4Z}{\pi a_0}J_1(q)\ , \tag{33}$$

where

$$J_1(q)=\frac{1}{\pi q^2}\int\frac{M_{\mathrm{NL}}(\vec{k}+\vec{q},\vec{k})\Theta^{<}(\vec{k})\Theta^{>}(\vec{k}+\vec{q})}{(\vec{k}+\vec{q})^2-k^2}\,d\vec{k}\ .$$

We symmetrize the integrand by the transformation $\vec{k}\rightarrow\vec{k}_-=\vec{k}-\vec{q}/2$ and $\vec{k}+\vec{q}\rightarrow\vec{k}_+=\vec{k}+\vec{q}/2$, use $\vec{q}$ as a polar axis, and write $\vec{k}\cdot\vec{q}=kq\mathrm{x}$ so that

$$J_1(q)=\frac{1}{q^3}\int\frac{dx}{x}\int M_{\mathrm{NL}}(\vec{k}_+,\vec{k}_-)\Theta^{<}(\vec{k}_-)\Theta^{>}(\vec{k}_+)\,k\,dk\ .$$

We now use the results of Geldart and Taylor[12] who have shown that, when the restrictions on the available phase space imposed by the $\Theta$ functions are allowed for, this integral takes the following form for

(i) $q\leqslant 2k_F$

$$J_1(q)=\frac{1}{q^2}\int_0^1 dx\int_0^1 ds\,kM_{\mathrm{NL}}(\vec{k}_+,\vec{k}_-)\ , \tag{34}$$

with

$$k=(s-\tfrac{1}{2})qx+k_F\left(1+\frac{q^2(x^2-1)}{4k_F^2}\right)^{1/2} \tag{35}$$

and (ii) $q \geqslant 2k_F$

$$J_1(q) = \frac{2k_F}{q^3}\int_{x_M}^{1}\left(1+\frac{q^2(x^2-1)}{4k_F^2}\right)^{1/2}\frac{dx}{x} \times \int_0^1 ds\, k\, M_{\mathrm{NL}}(\vec{k}_+,\vec{k}_-), \tag{36}$$

with

$$k = \frac{qx}{2} + (2s-1)k_F\left(1+\frac{q^2(x^2-1)}{4k_F^2}\right)^{1/2} \tag{37}$$

and

$$\chi_M = \left(1-\frac{4k_F^2}{q^2}\right)^{1/2}. \tag{38}$$

These integrals can easily be evaluated numerically. Thus combining Eqs. (10) and (33) we find that

$$\delta n(q) = -\frac{4\pi Z e^2}{q^2} M_{\mathrm{L}}(q)\chi(q) - \frac{4Z}{\pi a_0} J_1(q)\frac{\chi(q)}{\Pi_0(q)}, \tag{39}$$

with $J_1(q)$ defined by Eqs. (34)–(38).

To evaluate the energy–wave-number characteristic $F(q)$ [Eq. (26)] we need to reduce $H_2(q)$ [Eq. (22)] to a suitable form. Using (32) and the same technique as described above, this is easily done. The result is

$$\Omega H_2(q) = \left(\frac{4\pi Z e^2}{q^2} M_{\mathrm{L}}(q)\right)^2 \Pi_0(q) + \frac{32 Z^2 e^2}{q^2 a_0} J_1(q) M_{\mathrm{L}}(q) + \frac{\hbar^2}{2m}\frac{8Z^2}{\pi a_0^2} J_2(q), \tag{40}$$

where for (i) $q \leqslant 2k_F$,

$$J_2(q) = \frac{4\pi}{q^4}\int_0^1 dx \int_0^1 ds\, k[M_{\mathrm{NL}}(\vec{k}_+,\vec{k}_-)]^2, \tag{41}$$

with $k$ given by Eq. (35). And (ii) $q \geqslant 2k_F$,

$$J_2(q) = \frac{8\pi k_F}{q^5}\int_{x_M}^{1}\left(1+\frac{q^2(x^2-1)}{4k_F^2}\right)^{1/2}\frac{dx}{x}\int_0^1 ds\, k[M_{\mathrm{NL}}(\vec{k}_+,\vec{k}_-)]^2, \tag{42}$$

with $k$ and $\chi_{\mathrm{M}}$ given by Eqs. (33) and (38), respectively. Finally, inserting Eqs. (33) and (40) into (26), we obtain

$$F(q) = \frac{4\pi e^2}{q^2}\chi(q) M_{\mathrm{L}}^2(q) + \frac{8}{a_0\pi} J_1(q) M_{\mathrm{L}}(q)\frac{\chi(q)}{\Pi_0(q)} + q^2\left(\frac{4}{a_0\pi}\right)^2\left[\frac{a_0 J_2(q)}{16} - \frac{J_1^2(q)}{4\pi e^2 \Pi_0(q)}\left(1-\frac{\chi(q)}{\Pi_0(q)}\right)\right]. \tag{43}$$

The corresponding result for the two-component system is

$$F^{\alpha\beta}(q) = \frac{4\pi e^2}{q^2}\chi(q) M_{\mathrm{L}}^{\alpha}(q) M_{\mathrm{L}}^{\beta}(q) + \frac{4}{a_0\pi}[J_1^{\alpha}(q) M_{\mathrm{L}}^{\beta}(q) + J_1^{\beta}(q) M_{\mathrm{L}}^{\alpha}(q)]\frac{\chi(q)}{\Pi_0(q)} + q^2\left(\frac{4}{a_0\pi}\right)^2\left[a_0\frac{J_2^{\alpha\beta}(q)}{16} - \frac{J_1^{\alpha}(q) J_1^{\beta}(q)}{4\pi e^2 \Pi_0(q)}\left(1-\frac{\chi(q)}{\Pi_0(q)}\right)\right], \tag{44}$$

where $J_2^{\alpha\beta}(q)$ takes the same form as Eqs. (41) and (42), with $[M_{\mathrm{NL}}(\vec{k}_+,\vec{k}_-)]^2$ replaced by $M_{\mathrm{NL}}^{\alpha}(\vec{k}_+,\vec{k}_-) M_{\mathrm{NL}}^{\beta}(\vec{k}_+,\vec{k}_-)$.

In the Appendix we list formulas for $M_{\mathrm{L}}(q)$ and $M_{\mathrm{NL}}(\vec{k}',\vec{k})$ using three different forms of model pseudopotential.

Finally, we would like to add a practical comment concerning the use of $F(q)$ and $F^{\alpha\beta}(q)$ when they are inserted into Eqs. (25) and (29), respectively. It is well known that these functions generally tend to zero slowly as $q$ tends to infinity, rendering the calculation of pair potentials rather tedious. A typical example is illustrated in Fig. 1 where it can be seen that $F(q)$ tends to oscillate for large $q$ as it goes asymptotically to zero. The minima for these oscillations are small and positive, though for a local pseudopotential they would be zero. We have found in practice that if the range of integration is terminated at one of these minima beyond $q = 2k_F$ no significant error occurs in the calculated pair potential. Using Al as an example truncation of $F(q)$ at the first minimum beyond $q = 2k_F$ gives an error in $V_{\mathrm{II}}(r_1)$ ($r_1$ is the first-neighbor distance) of about $3\times 10^{-5}$ Ry. and at the second minimum less than $10^{-5}$ Ry. For the alkali metals we have found the errors to be considerably smaller. They also appear to be roughly independent of choice of screening or pseudopotential. Hence the long-range oscillations in $F(q)$ have no significant influence on the pair potential in the range of physical interest and can be safely ignored particularly if $F(q)$ is truncated at the second minimum beyond $q = 2k_F$.

## IV. NUMERICAL APPLICATION TO SODIUM

In an earlier paper[13] we used a local pseudopotential to calculate the charge densities induced

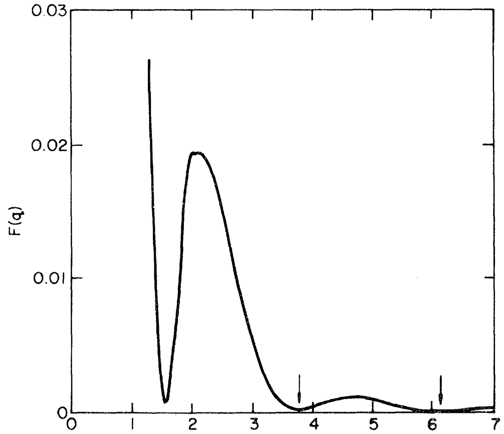

FIG. 1. A typical example of the large-$q$ behavior of $F(q)$ calculated using a nonlocal model potential for Al. Points where $F(q)$ may be truncated are indicated by arrows.

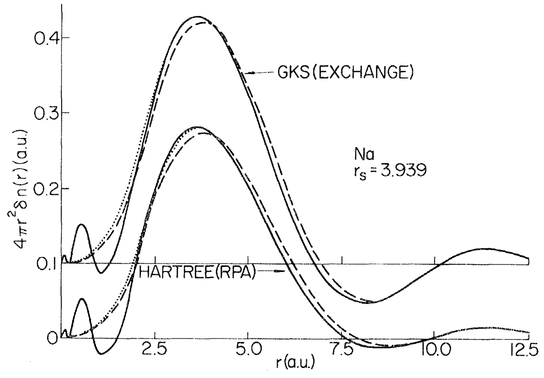

FIG. 2. Charge densities induced by an isolated Na$^+$ ion in an electron gas. For clarity the GKS exchange results are displaced upwards by 0.1 a.u. relative to the Hartree results; solid line, Dagens' (1972) self-consistent calculations; dashed line, linear-response calculation with model potential $M1$; dotted line, linear-response calculation with model potential $M2$.

by isolated Na$^+$ and Li$^+$ ions and compared them with Dagens'[5] self-consistent results. In the Na case the agreement between the two calculations seemed to be quite satisfactory and we concluded that nonlinear effects were not significant. However, later calculations have proven that this is not the case, and hence we feel that it is instructive to reexamine the Na case in detail using a nonlocal pseudopotential. The Li situation is not so straightforward as Na and will be discussed in a later paper.[7]

For our calculations we have chosen a nonlocal model potential of the form of Eq. (A6) in the Appendix. Choosing the parameters $A_0 = -0.439$ Ry., $A_2 = -1.40$ Ry., $R_0 = 2.21$ a.u., and $R_1 = 2.26$ a.u., which we shall refer to as model potential $M1$, we have evaluated the phase shifts as functions of $r$ at the Fermi energy. These are listed in Table I from which it can be seen that the $M1$ model potential gives phase shifts agreeing very well with those generated by the Prokofjew[14] Na$^+$ potential for $r \gtrsim 2.2$ a.u. This model potential then is formally equivalent to the Prokofjew potential in that region.

TABLE I. Comparison of the Na phase shifts, calculated using model potential $M1$, with ionic-potential phase shifts at the Fermi energy.

| $r$ | Model Potential | | | Ionic Potential | | |
|---|---|---|---|---|---|---|
| (a.u.) | $\delta_s$ | $\delta_p$ | $\delta_d$ | $\delta_s$ | $\delta_p$ | $\delta_d$ |
| 2.0 | 0.000 | 0.000 | 0.0001 | −0.114 | −0.005 | 0.0001 |
| 2.2 | 0.000 | 0.000 | 0.0001 | −0.027 | −0.002 | 0.0001 |
| 2.4 | 0.111 | 0.003 | 0.0002 | 0.093 | 0.002 | 0.0002 |
| 2.6 | 0.261 | 0.008 | 0.0003 | 0.248 | 0.007 | 0.0003 |
| 2.8 | 0.437 | 0.013 | 0.0004 | 0.430 | 0.013 | 0.0004 |
| 3.0 | 0.621 | 0.020 | 0.0005 | 0.618 | 0.020 | 0.0005 |
| 3.2 | 0.790 | 0.028 | 0.0007 | 0.788 | 0.028 | 0.0007 |
| 3.4 | 0.928 | 0.037 | 0.0009 | 0.927 | 0.037 | 0.0009 |
| 3.6 | 1.032 | 0.046 | 0.0011 | 1.032 | 0.045 | 0.0011 |
| 3.8 | 1.105 | 0.054 | 0.0013 | 1.105 | 0.054 | 0.0013 |
| 4.0 | 1.152 | 0.062 | 0.0015 | 1.153 | 0.062 | 0.0015 |

In order to make a comparison with Dagens' results it is necessary to know which approximation to $\Pi(q)$ is appropriate to insert into Eqs. (12) and (39). Dagens performed two calculations, one using just a Hartree self-consistent field and the other including Gasper-Kohn-Sham (GKS) exchange as well. In the linear-response approximation $\Pi_0(q)$ Eq. (14) is formally equivalent to the Hartree approximation, and the following $\Pi(q)$ is formally equivalent to the GKS exchange approximation[13]

$$\Pi_x(q) = \frac{\Pi_0(q)}{1 - \pi e^2 \Pi_0(q)/k_F^2} \; . \tag{45}$$

Using both $\Pi_0(q)$ and $\Pi_x(q)$ we have calculated $\delta n(q)$ [Eq. (39)] and its Fourier transform

$$\delta n(r) = \frac{1}{(2\pi)^3} \int \delta n(q) e^{i\vec{q}\cdot\vec{r}} d\vec{q} \tag{46}$$

which in each case is compared with Dagens' calculations in Fig. 2. The agreement appears to be quite good. However, by adjusting the model-potential parameters to the values $A_0 = -0.439$ Ry., $A_2 = -1.40$ Ry., $R_0 = 2.08$ a.u., and $R_1 = 2.00$ a.u. which we shall refer to as $M2$, the $\delta n(r)$ curves can be made to coincide almost exactly with those of Dagens in both cases for $r \gtrsim 2.5$ a.u. as can be seen from the figure.

Turning now to the energy–wave-number characteristic $F(q)$ [Eq. (43)], we have used both model potentials $M1$ and $M2$ to calculate this quantity. In this instance we used the Geldart and Taylor[15] version of $\Pi(q)$, which includes correlations. The phonon dispersion curves which were generated from $F(q)$ in each case are compared with the experimental values of Woods *et al.*[16] in Fig. 3. It is quite clear from this figure that the $M1$ curves are not at all satisfactory, containing, in some instances, errors $\gtrsim 10\%$, whereas the $M2$ curves agree very well indeed. From these results we are able to draw two important conclusions. First nonlinear effects are important in Na and therefore they are most probably important in all metals. Second we can correct for these nonlinear effects in a consistent fashion by suitable adjustments to the model-potential parameters. Thus we are able to retain the essential simplicity of the pseudopotential approach and still remain confident that the calculations are meaningful. It still is necessary to show that these conclusions can be generalized to other materials. Preliminary calculations in K and Al give similar results and these will be reported in a later publication.[7]

Let us now turn our attention to the actual interionic potentials generated by $M1$ and $M2$. These are illustrated in Fig. 3. The effect of the nonlinear correction is to deepen the first well of the potential and to move its position in the direction of smaller $r$. A characteristic feature of interionic potentials is the presence of the long-range oscillations which are manifestations of the Friedel oscillations in the charge density. Since even the first well is basically a Friedel oscillation, it is necessary to get the amplitude of the oscillations right. This of course is easily achieved by fitting the pseudopotential to the charge density. Fitting to elastic constants or to phonon dispersion curves does not give a unique oscillation amplitude as is well known (e.g., see Duesbery and Taylor[17]). This serves as another illustration of the main theme of this paper, i.e., that the charge density plays a central role in the determination of the dynamic properties of the lattice.

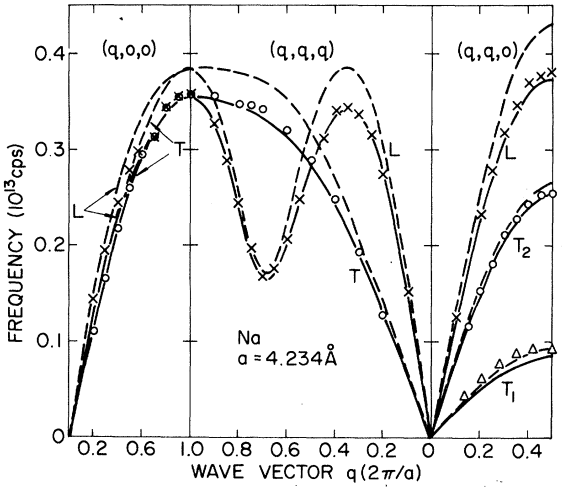

FIG. 3. Phonon dispersion curves for Na. The experimental points which are taken from Woods *et al.* (Ref. 16) are indicated by × for longitudinal branches and by ○ and △ for transverse branches. Dashed line represents $M1$ model potential; solid line $M2$ model potential.

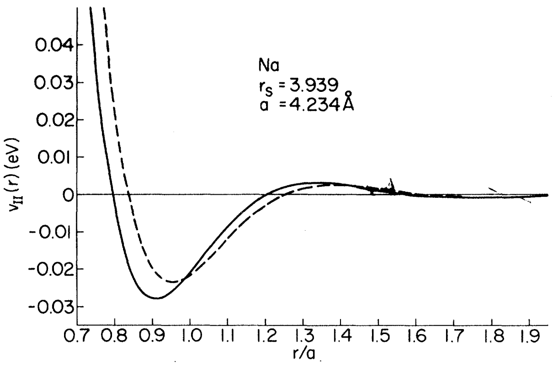

FIG. 4. Interionic potential for Na calculated using the $M1$ model potential (dashed line) and the $M2$ model potential (solid line).

As a final comment in this section it is interesting to note that in the near-neighbor region the interionic potential generated by model potential $M2$ agrees very well with that of Basinski *et al.*,[18] who used an orthogonalized plane wave model. For larger values of $r$ ($r > 1.2a$) the oscillation amplitude of the $M2$ potential is about 30% less than that of Basinski *et al.* In view of the above comments it seems most likely that the $M2$ potential is the more nearly correct one.

## V. SUMMARY AND CONCLUSIONS

The principal point that we have emphasized in this paper is that the charge density is of central importance in calculating the cohesive energy and thus should be used to guide us in constructing meaningful interionic potentials. With this in mind we have used, as a starting point for the formalism in Sec. II, the HKS equations, which are based on the fact that the energy can be expressed as a functional of the density.[2] Taking the limit of a vanishingly small potential we have derived the linear-response result for the charge density including nonlocal effects and exchange and correlation. The same formalism was then applied to the problem of the cohesive energy of a random array of ions from which we extracted the energy–wave-number characteristics and the interionic potential. The results are presented in a numerically useful form in Eqs. (39), (43), and (44).

By making a careful comparison with Dagens'[15] Na self-consistent charge-density calculations we have been able to show that despite the fact that the linear-response results appear to agree quite well with them, the nonlinear terms are still very significant. However by adjusting the pseudopotential parameters to bring the linear-response results into coincidence with the self-consistent charge density, we are able to simulate the nonlinear effects. This fact provides a very good justification for the standard pseudopotential treatment of the properties of liquid metals, defect systems, and perfect crystals. This is an important point since (e.g., see Wiser and Greenfield[1]) the explicit inclusion of higher-order terms makes the problem much more complicated. It also follows that a necessary and perhaps sufficient prerequisite to the generation of a reliable interionic potential is the generation of an accurate charge density.

As we have stated before in this paper our results do not appear to be an artifact of Na but appear to be of a general nature, and calculations extended to other simple metals will be published later.[7]

## ACKNOWLEDGMENTS

One of us (R. T.) would like to thank the Theoretical Physics Division, A. E. R. E. Harwell for their hospitality during the time when this work was completed.

## APPENDIX

In Sec. III we found it convenient to split the matrix element $\langle\vec{k}+\vec{q}\,|\hat{v}_p|\,\vec{k}\rangle$ into a local and a nonlocal part. These are defined in Eq. (32), which we rewrite here:

$$\langle\vec{k}+\vec{q}\,|\hat{v}_p|\,\vec{k}\rangle = \frac{4\pi Ze^2}{\Omega q^2}[M_L(q)+M_{NL}(\vec{k}+\vec{q},\vec{k})]\,. \quad (32)$$

The evaluation of $\delta n(q)$, $F(q)$, and $F^{\alpha\beta}(q)$ via Eqs. (39), (43), and (44), respectively, requires knowledge of both $M_L$ and $M_{NL}$. In this Appendix we list formulas for these quantities for three different model potentials, all of which are of the form

$$\hat{v}_p = \sum_l \left(A_l\Theta(R_l - r) - \frac{Ze^2}{r}\Theta(r-R_l)\right)\hat{P}_l\ ,$$

where $\Theta(x)$ is the usual step function and $\hat{P}_l$ is the angular momentum projection operator.

$$\text{(i)}\quad \hat{v}_p = \left[-\frac{Ze^2}{r}+\left(A_0+\frac{Ze^2}{r}\right)\Theta(R_M - r)\right]\hat{P}_0, \quad (l=0)$$
$$= \left[-\frac{Ze^2}{r}+\left(A_1+\frac{Ze^2}{r}\right)\Theta(R_M - r)\right]\hat{P}_1, \quad (l=1)$$
$$= \left[-\frac{Ze^2}{r}+\left(A_2+\frac{Ze^2}{r}\right)\Theta(R_M - r)\right]\hat{P}_l, \quad (l\geqslant 2). \qquad \text{(A1)}$$

This is the usual Heine-Abarenkov[19] model potential for which

$$M_L(q) = \frac{A_2R_M}{Ze^2}\,\frac{\sin qR_M}{qR_M} - \left(\frac{A_2R_M}{Ze^2}+1\right)\cos qR_M\ , \qquad \text{(A2)}$$

$$M_{NL}(\vec{k}',\vec{k}) = q^2\left(\frac{(A_0-A_2)}{Ze^2}K_0(k',k,R_M) + 3\cos\theta\,\frac{(A_1-A_2)}{Ze^2}K_1(k',k,R_M)\right)\ , \qquad \text{(A3)}$$

where $\theta$ is the angle between $\vec{k}'$ and $\vec{k}$

$$K_l(k',k,R) = \int_0^R r^2 j_l(k'r)\,j_l(kr)\,dr$$

and $j_l(\rho)$ is the spherical Bessel function of order $l$.

$$K_0(k',k,R) = \left(\frac{\sin kR}{k}\cos k'R - \frac{\sin k'R}{k'}\cos kR\right)\Big/(k^2-k'^2)\ ,\ (k\neq k')$$
$$= \frac{2kR-\sin 2kR}{4k^3} + \frac{\Delta k}{8k^4}[3\sin 2kR - 2kR(2+\cos 2kR)] + O((\Delta k)^2)\ , \quad (k'=k+\Delta k) \qquad \text{(A4)}$$

$$K_1(k',k,R) = \frac{R}{k^2-k'^2}[\,j_1(kR)\sin k'R - j_1(k'R)\sin kR\,]\ , \quad (k\neq k')$$
$$= \left(-\frac{R}{k^2}j_1(kR)\sin kR + \frac{2kR-\sin 2kR}{4k^3}\right)\left(1-\frac{2\Delta k}{k}\right) + \frac{\Delta k}{8k^4}[-3\sin 2kR + 2kR(2+\cos 2kR)] + O((\Delta k)^2)\ ,$$
$$(k'=k+\Delta k) \qquad \text{(A5)}$$

$$\text{(ii)}\quad \hat{v}_p = \left[-\frac{Ze^2}{r}+\left(A_0+\frac{Ze^2}{r}\right)\Theta(R_0 - r)\right]\hat{P}_0, \quad (l=0)$$
$$= \left[-\frac{Ze^2}{r}+\left(A_0+\frac{Ze^2}{r}\right)\Theta(R_1 - r)\right]\hat{P}_1, \quad (l=1) \qquad \text{(A6)}$$
$$= \left[-\frac{Ze^2}{r}+\left(A_2+\frac{Ze^2}{r}\right)\Theta(R_1 - r)\right]\hat{P}_l, \quad (l\geqslant 2).$$

This form of model potential follows quite naturally from the variable phase shift approach.[6] In this case

$$M_L(q) = \frac{R_1A_2}{Ze^2}\,\frac{\sin qR_1}{qR_1} - \left(\frac{R_1A_2}{Ze^2}+1\right)\cos qR_1\ , \qquad \text{(A7)}$$

$$M_{\mathrm{NL}}(\vec{\mathrm{k}}',\vec{\mathrm{k}})=q^2\biggl(\frac{A_0}{Ze^2}K_0(k',k,R_0)-\frac{A_2}{Ze^2}K_0(k',k,R_1)+3\cos\theta\,\frac{(A_0-A_2)}{Ze^2}K_1(k',k,R_1)+\frac{I(k+k',R_0,R_1)-I(|k-k'|,R_0,R_1)}{2kk'}\biggr)\,, \tag{A8}$$

where

$$I(k,R_1,R_1)=\int_{kR_0}^{kR_1}\cos\rho\,\frac{d\rho}{\rho}$$

and $K_0$ and $K_1$ are defined by Eqs. (A4) and (A5).

$$\text{(iii)}\quad v_p=\left[-\frac{Ze^2}{r}+\left(A_0+\frac{Ze^2}{r}\right)\Theta(R_0-r)\right]\hat{P}_0,\quad (l=0)$$

$$=\left[-\frac{Ze^2}{r}+\left(A_1+\frac{Ze^2}{r}\right)\Theta(R_1-r)\right]\hat{P}_1,\quad (l=1)$$

$$=-\frac{Ze^2}{r}\hat{P}_l\,,\qquad (l\geqslant 2)\,. \tag{A9}$$

A particular version of this model potential is that due to Shaw[20] for which $A_l=-Ze^2/R_l$. In this case

$$M_{\mathrm{L}}(q)=-1\,, \tag{A10}$$

$$M_{\mathrm{NL}}(\vec{\mathrm{k}}',\vec{\mathrm{k}})=q^2\left[\frac{A_0}{Ze^2}K_0(k',k,R_0)+J_0(k',k,R_0)+3\cos\theta\left(\frac{A_1}{Ze^2}K_1(k',k,R_1)+J_1(k',k,R_1)\right)\right]\,, \tag{A11}$$

where $K_0$ and $K_1$ are again given by Eqs. (A4) and (A5) and

$$J_l(k',k,R)=\int_0^R rj_l(k'r)\,j_l(kr)\,dr\,,$$

$$J_0(k',k,R)=\frac{1}{2kk'}\left(\ln\left|\frac{k+k'}{k-k'}\right|-\frac{1}{2kk'}\int_{|k-k'|R}^{(k+k')R}\cos\rho\,\frac{d\rho}{\rho}\right),\quad (k\neq k')$$

$$=\left(\frac{1}{2k^2}\int_0^{2kR}(1-\cos\rho)\frac{d\rho}{\rho}\right)\left(1-\frac{\Delta k}{k}\right)+\frac{\Delta k}{k}\,\frac{(1-\cos 2kR)}{4k^2}+O((\Delta k)^2)\,,\quad (k'=k+\Delta k) \tag{A12}$$

$$J_1(k',k,R)=-\frac{1}{2kk'}[1+kk'R^2j_1(kR)\,j_1(k'R)-\cos kR\cos k'R]+\frac{(k^2+k'^2)}{2kk'}J_0(k',k,R)\,. \tag{A13}$$

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