

Pseudopotential Theory of Metallic Lithium*

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A detailed calculation of the electronic structure of a screened lithium ion is made, with a view to testing some of the assumptions and approximations which have been used in pseudopotential work. Within the confines of a linearly screened Austin pseudopotential we conclude that for lithium, (i) the Slater approximation in the treatment of core-valence exchange is qualitatively incorrect, (ii) the phase shifts considerably overestimate the screening charge, and (iii) the core states are little different from those of the free ion. It is emphasized that when calculating the form factor, it is better to use the Born approximation, which automatically scales by describing the forward scattering correctly, than to use approximate phase shifts which violate significantly the Friedel sum rule.

I. INTRODUCTION

SINCE the pioneering work of Phillips and Kleinman,¹ also Antončík,² a considerable literature has accumulated on the theory of pseudopotentials.³ The extension of the theory to metals came a little later because of difficulties associated with self-consistent screening, and particularly central to this development have been the important contributions of Cohen and Heine,⁴ Cohen and Phillips,⁵ and Harrison.^{6,7}

Using a linear screening approach, it has been shown that for simple metals one may break down the many-ion problem to that associated with a single ion immersed in an electron gas. This proposition is stated most clearly in the recent review by Ziman,⁸ who refers to the screened ion thus obtained as a neutral pseudo-atom. In the present work, we investigate the structure of a lithium pseudo-atom.

Our calculations were carried out in the spirit of the concluding remarks of Ref. 8, our aim being to take a simple system for which no approximation of a non-essential nature is necessary, and to test the validity of some of the assumptions and approximations which have hitherto been employed. For mathematical convenience, we chose the Austin^{9,10} rather than the "best" Harrison form of pseudopotential and then linearly screened it. In this way, we introduced what were regarded, together with the restricted orbital forms (2) below, as the essential approximations. No subsequent mathematical

approximation of any substance was thereafter necessary. Within the framework of this model we investigated (i) the degree of necessity for screening the core-valence exchange operator, (ii) the Slater approximation¹¹ to the latter, (iii) the assumption that the core states are as in the free atom (ion), (iv) the reduction of the screened pseudopotential to semilocal⁴ form, and (v) the role of Born approximation in describing the scattering.

The above matters are conveniently tackled by discussions of Hartree screening in Sec. II and core-valence exchange in Sec. III. This is followed, in Sec. IV, by explicit evaluation of wave functions and potentials in direct space. In Sec. V, the effect of varying the core size is investigated, and finally, in Sec. VI, our conclusions are given.

II. HARTREE-BORN CALCULATIONS

We study here, in the Hartree approximation, the problem of a lithium ion immersed in an electron gas. This is a natural generalization of the work of March and Murray¹² on the screening of point charges by free electrons, to the case when bound states are explicitly allowed for. Thus, the valence-electron Schrödinger equations are written in the form

$$(-\frac{1}{2}\nabla^2 + U + U_s)\psi = \mathcal{E}\psi, \quad (1)$$

where U and U_s are the Hartree fields associated with the core and valence electrons, respectively. (Unless otherwise stated, atomic units will be used throughout this work.)

We now make the assumption that the core orbitals are described by Slater-type forms¹³

$$\Psi(r) = (\alpha^3/\pi)^{1/2} e^{-\alpha r}. \quad (2)$$

If we choose $\alpha = 2.69$, then, within this approximation, the core functions are those of the free ion. Using (2),

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¹ J. C. Phillips and L. Kleinman, *Phys. Rev.* **116**, 287 (1959).

² E. Antončík, *J. Phys. Chem. Solids* **10**, 314 (1959).

³ The subject has been recently reviewed by L. J. Sham and J. M. Ziman, *Solid State Phys.* **15**, 221 (1963). We would like to thank Dr. Sham for useful advice about work in progress when this investigation was begun.

⁴ M. H. Cohen and V. Heine, *Phys. Rev.* **122**, 1821 (1961).

⁵ M. H. Cohen and J. C. Phillips, *Phys. Rev.* **124**, 1818 (1961).

⁶ W. A. Harrison, *Phys. Rev.* **129**, 2503 (1963); **129**, 2512 (1963); **136**, A1107 (1964).

⁷ W. A. Harrison, *Phys. Rev.* **131**, 2433 (1963).

⁸ J. M. Ziman, *Advan. Phys.* **13**, 89 (1964).

⁹ B. J. Austin, V. Heine, and L. J. Sham, *Phys. Rev.* **127**, 276 (1962).

¹⁰ F. Bassani and V. Celli, *J. Phys. Chem. Solids* **20**, 64 (1961).

¹¹ J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

¹² N. H. March and A. M. Murray, *Phys. Rev.* **120**, 830 (1960); *Proc. Roy. Soc. (London)* **A261**, 119 (1961); **A266**, 559 (1962).

¹³ See, for example, N. F. Mott and I. N. Sneddon, *Wave Mechanics and Its Applications* (Clarendon Press, Oxford, England, 1948), p. 144.

the core potential is directly evaluated to be [see Appendix, part (i)]

$$U = -\frac{1}{r} - \frac{2}{r} e^{-2\alpha r} - 2\alpha e^{-2\alpha r}. \quad (3)$$

The screening potential U_S , on the other hand, is defined in terms of the valence-electron wave functions. It will be evaluated self-consistently below.

Cohen and Heine⁴ have shown how to replace (1), with its attendant core-orthogonality requirements, by

$$(-\frac{1}{2}\nabla^2 + U + U_R + U_S)\phi = \mathcal{E}\phi, \quad (4)$$

the latter having no such subsidiary conditions. Here, each ϕ is the "smooth part" of the corresponding ψ , the explicit relationship being

$$\psi = \phi - \langle \phi | \Psi \rangle \Psi. \quad (5)$$

The operator U_R is sufficiently repulsive to remove all bound states from (1), and the usual assumption is that the resulting net potential is weak enough to treat by low-order perturbation theory.

On account of a certain arbitrariness in the definition (5), where, it will be noted, ϕ is not defined within an additive multiple of Ψ , there is some flexibility in our choice of U_R . Harrison's choice^{6,7} was made so as to minimize the net potential and thus to maximize the efficiency of the perturbation method. Unfortunately, such a choice of operator is so complicated that it would appear to preclude any possibility of transcending the first Born approximation in calculating the differential scattering cross section. We have, therefore, taken the Austin^{9,10} form defined by

$$U_R\phi = -\langle \Psi | U | \phi \rangle \Psi, \quad (6)$$

which subsequently allows us to perform a partial-wave analysis. In practice (say in low-order perturbation theory), the difference between the Harrison and Austin forms might be anticipated to be small,^{4,9} and certainly our results below are not in conflict with such an expectation.¹⁴ In principle (i.e., if exact solutions were obtainable), a theorem due to Austin, Heine, and Sham⁹ guarantees that the scattering should be properly described by either choice, though the clearcut nature of that result is somewhat muddled in the case of metals because of the self-consistent screening which is necessary.

Solving (4) in linear approximation leads to^{6,7}

$$U_S(q) = \frac{8\pi}{q^2 \epsilon(q)} \frac{2}{(2\pi)^3} \times \int_{k < k_F} d^3k \frac{\langle \mathbf{k} + \mathbf{q} | U + U_R | \mathbf{k} \rangle}{E_k - E_{\mathbf{k} + \mathbf{q}}}, \quad E_k = \frac{1}{2}k^2, \quad (7)$$

¹⁴ But we should remark that Dr. Harrison has indicated to us that this is perhaps not the case in aluminum.

for the screening in momentum space, where $\epsilon(q)$ is the usual Hartree dielectric function. From (5), (6), and (7) the matrix elements for the net potential are now given by

$$\langle \mathbf{k} + \mathbf{q} | U + U_R + U_S | \mathbf{k} \rangle = U(q) - \langle \mathbf{k} + \mathbf{q} | \Psi \rangle \langle \Psi | U | \mathbf{k} \rangle + U_S(q). \quad (8)$$

Thus, the scattering at the Fermi surface in Born approximation, described by

$$u(q) = [\langle \mathbf{k} + \mathbf{q} | U + U_R + U_S | \mathbf{k} \rangle]_{k=|\mathbf{k} + \mathbf{q}|=k_F}, \quad (9)$$

is readily obtained using (8).

For convenience, we reserve comment on our results till Sec. III.

III. CORE-VALENCE EXCHANGE

Harrison^{6,7} has used the Slater averaging method¹¹ in an effort to include core-valence exchange. We find that in the present case this procedure leads to an incorrect result. To prove this statement, the appropriate matrix elements are calculated first of all exactly, and then in Slater approximation. The details are as follows.

Let us suppose our core potential U is now replaced by $U + A$, where A is a core-valence exchange operator. Because of linearity, the development of Sec. II is readily generalized. In fact, all equations remain the same except (1), which becomes

$$(-\frac{1}{2}\nabla^2 + U + U_S + A + A_S)\psi = \mathcal{E}\psi, \quad (10)$$

and (4), which becomes

$$(-\frac{1}{2}\nabla^2 + U + U_R + U_S + A + A_R + A_S)\phi = \mathcal{E}\phi, \quad (11)$$

where

$$A_R\phi = -\langle \Psi | A | \phi \rangle \Psi, \quad (12)$$

and

$$A_S(q) = \frac{8\pi}{q^2 \epsilon(q)} \frac{2}{(2\pi)^3} \int_{k < k_F} d^3k \frac{\langle \mathbf{k} + \mathbf{q} | A + A_R | \mathbf{k} \rangle}{E_k - E_{\mathbf{k} + \mathbf{q}}}. \quad (13)$$

Thus A_S is the modification to the *Hartree* field of the valence electrons brought about by the introduction of core-valence exchange. The matrix element appropriate to Born scattering is now

$$w(q) = u(q) + a(q), \quad (14)$$

where

$$a(q) = [\langle \mathbf{k} + \mathbf{q} | A + A_R + A_S | \mathbf{k} \rangle]_{k=|\mathbf{k} + \mathbf{q}|=k_F}. \quad (15)$$

We have computed (15) for A defined properly in what will be called the Dirac form

$$A\phi(\mathbf{r}) \equiv A^D\phi(\mathbf{r}) = -\Psi(r) \int \frac{d^3r'}{|\mathbf{r} - \mathbf{r}'|} \Psi^*(\mathbf{r}')\phi(\mathbf{r}'), \quad (16)$$

and find its effect, through (14), is to raise the corresponding Hartree result (9) so as to give a larger posi-

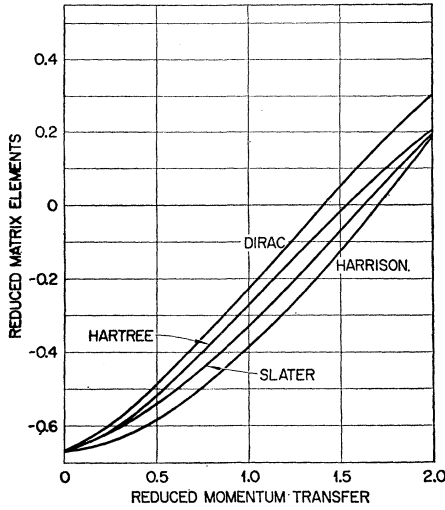


FIG. 1. Reduced matrix element, $2\pi f(q)/\Omega_0 E_F$ in various approximations, versus reduced momentum transfer q/k_F . The Hartree curve arises from Eq. (9), the Dirac from (14) and (16), and the Slater from (14) and (17). Harrison's curve is taken from Ref. 7.

tive intercept at $q=2k_F$. However, just as Harrison found on choosing A in Slater form, in this case as

$$A \equiv A^S = -3\{(3/4\pi)\Psi^2\}^{1/3}, \quad (17)$$

the Hartree curve is lowered. The situation is illustrated in Fig. 1 for $k_F=0.578$, appropriate to the liquid at its melting point, and for $\alpha=2.69$, the free-ion value. Also included is a graph drawn from Harrison's published data,⁷ which corresponds to a 3% higher k_F . After normalizing as indicated, it should nevertheless, be directly comparable with our curve calculated using Slater approximation. The agreement is quite good and is consistent with the view that the Austin pseudopotential approximates well to the Harrison form, though it should be pointed out that this is by no means proved, as the choices of core orbital were also different.¹⁴ Our use of (2) was dictated by a desire to obtain at every stage, closed form expressions in α and k_F , with the eventual intention of self-consistently applying them to solids,¹⁵ liquids,^{8,15,16} and compressed vapors.¹⁷

Let us characterize each curve in Fig. 1 by a number, namely, the resistivity, calculated from the formula^{8,15,17}

$$\rho = k_F \int_0^\pi \alpha(q) |f(q)|^2 (1 - \cos\theta) 2\pi \sin\theta d\theta, \quad (18)$$

$$q = 2k_F \sin\frac{1}{2}\theta.$$

Here, $\alpha(q)$ is the ion-ion structure factor, given, for

¹⁵ G. Baym, Phys. Rev. **135**, A1691 (1964); M. P. Greene and W. Kohn, Phys. Rev. **137**, A513 (1965).

¹⁶ J. M. Ziman, Phil. Mag. **6**, 1013 (1961); C. C. Bradley, T. E. Faber, E. G. Wilson, and J. M. Ziman, Phil. Mag. **7**, 865 (1962).

¹⁷ W. H. Young, Phys. Letters **8**, 253 (1964); Axel Meyer, C. W. Nestor, Jr., and W. H. Young, Phys. Rev. **138**, A1591 (1965).

liquid lithium at its melting point, by the experimental data of Gingrich and Heaton,¹⁸ and $f(q)$ is the scattering amplitude at any one site for electrons at the Fermi level. In Born approximation we may use (9) and (14) instead of $2\pi f(q)$, and in this way calculate values for the resistivities. These, together with the experimental observations,¹⁹ are shown in Table I. It is clear that

TABLE I. Born resistivities appropriate to the liquid at its melting point, calculated in various approximations, compared with the experimental results. Because of the different k_F employed, we have adjusted the Harrison resistivity upward by 3%. Despite the latter's favorable comparison with experiment, it is the Dirac value which is more properly based theoretically. It should be remembered, however, that even small errors in the neutron scattering data could quite seriously affect the calculated numbers.

	Hartree	Dirac	Slater	Harrison	Clayton and Enderby (experimental)	Freedman and Robertson (experimental)
ρ ($\mu\Omega$ cm)	27.8	61.3	24.9	25.4	25.3	24.0

the Slater method leads to a misleadingly good result in Born approximation.

The source of the contrasting behavior resulting from the use of A^D and A^S may be traced by analyzing the various components of (15) in the two calculations. For this purpose, let us write²⁰

$$a^0 = a_0^0 + A_S^0, \quad a_0^0 = [\langle \mathbf{k} + \mathbf{q} | A | \mathbf{k} \rangle]_{k=|\mathbf{k}+\mathbf{q}|=k_F}, \quad (19)$$

and

$$a^R = a_0^R + A_S^R, \quad a_0^R = [\langle \mathbf{k} + \mathbf{q} | A_R | \mathbf{k} \rangle]_{k=|\mathbf{k}+\mathbf{q}|=k_F}, \quad (20)$$

so that by an obvious decomposition, (13) reads

$$A_S = A_S^0 + A_S^R, \quad (21)$$

and now (15) becomes

$$a = a^0 + a^R. \quad (22)$$

Thus, in (19) and (20), a suffix zero is added to a screened matrix element to denote its unscreened counterpart.

The various components have been plotted in Fig. 2. It will be seen that in the vitally important large-angle scattering region, where the angle factors and ion-ion correlation functions combine to magnify small differences, the Slater and Dirac forms of a^0 are rather similar, but the agreement is much poorer in the case of the a^R . It is clear from the graphs that the differences in the latter arise from the ceiling values a_0^R to which they climb, suggesting that the Slater averaging method

¹⁸ N. S. Gingrich and L. Heaton, J. Chem. Phys. **34**, 873 (1961). We wish to thank Dr. Heaton for supplying us with further details on this work.

¹⁹ N. Cusack, Rept. Progr. Phys. **26**, 361 (1963). See Table I.

²⁰ More details will be found in the Appendix, parts (iii) and (iv).

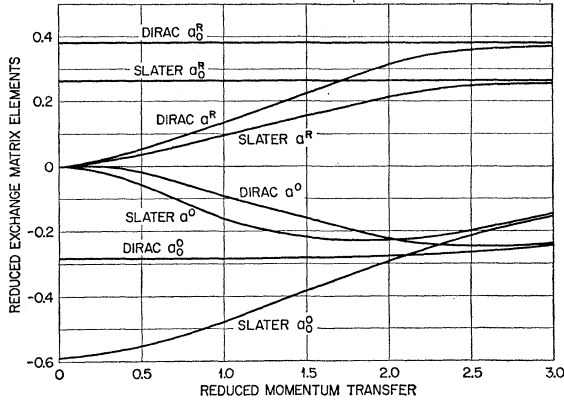


FIG. 2. Unscreened and screened exchange matrix elements versus reduced momentum transfer q/k_F . For precise definitions of the a 's, see Eqs. (19)–(22) inclusive. Each term is calculated in two approximations, one (Dirac) appropriate to (16) and the other (Slater) appropriate to (17). Beyond $q=2k_F$, the curves are not physically meaningful, but help to illustrate the mathematical point discussed in the paragraph following Eq. (22).

is not particularly applicable to the evaluation of matrix elements of the type $\langle \Psi | A | \mathbf{k} \rangle$, which arise in the pseudopotential method. Explicitly, in the present case, a little algebra gives [see (A29) and (A30)]

$$\langle \Psi | A^D | \mathbf{k} \rangle = -4\pi(\alpha^3/\pi)^{1/2}[(\alpha^2+k^2)^{-1} + 2(9\alpha^2+k^2)^{-1} + 12\alpha^2(9\alpha^2+k^2)^{-2}], \quad (23)$$

and [see (A36)]

$$\langle \Psi | A^S | \mathbf{k} \rangle = -4\pi(\alpha^3/\pi)^{1/2} \times 10\alpha^2(3/4\pi^2)^{1/3}[(25\alpha^2/9)+k^2]^{-2}. \quad (24)$$

The analytic nature of (23) is changed, the transformed exponential in (24) not approximating very well to the dominant screened Coulomb transform in (23).

It might also be noted that Fig. 2 indicates that the effect of screening on the core-valence exchange operator is not negligible. This seems to be at variance with a conclusion concerning small-core systems reached by Cohen and Phillips⁵ using general arguments.

Because of our difficulties with exchange, we revert, in what follows, to the *Hartree* method of Sec. II. What, then, is the status of the matrix element (9)? As we have seen, it predicts the resistivity quite well. Probably it provides a very reasonable description of the scattering. Nevertheless, considerations below indicate that certain difficulties still remain.

IV. PARTIAL-WAVE ANALYSIS

We are now in a position to perform a partial-wave analysis. In this way, below, we calculate a screened pseudopotential in direct space, the corresponding wave functions, and the associated phase shifts. Thus, we are able to discuss points (iii)–(v) raised in Sec. I.

The radial Schrödinger equations resulting from (1)

are of the standard type

$$\left[-\frac{1}{2r} \frac{d^2}{dr^2} r + U + U_s + \frac{l(l+1)}{2r^2} \right] R_l = \mathcal{E} R_l. \quad (25)$$

In a similar way, bearing in mind that (6) vanishes if ϕ is a spherical harmonic not of s type, (4) reduces to (25) for $l \neq 0$, while for s waves we obtain

$$\left[-(1/2r)(d^2/dr^2)r + U + U_s \right] R_0 - \langle \Psi | U | R_0 \rangle \Psi = \mathcal{E} R_0. \quad (26)$$

These equations have been solved²¹ using a U_s obtained by Fourier transforming (7), and for \mathcal{E} having first the value zero and then the free-electron Fermi energy $\frac{1}{2}k_F^2$. All our results below, both in this and subsequent sections, are for the liquid at its melting point ($k_F=0.578$). In addition, in the present section, we confine our attention to the free-ion case $\alpha=2.69$.

First of all, let us consider the two s -wave solutions at the Fermi level, these being represented as in Fig. 3. That for (26) is found exactly by direct solution; that for (25) is obtained approximately and indirectly by using (5). At large distances the two curves merge, and we obtain a common s -wave phase shift η_0 (modulo 2π) and a common scattering amplitude for (1) and (4), given by

$$f(q) = (2ik_F)^{-1} \sum_0^{\infty} (2l+1)(e^{2i\eta_l} - 1) P_l(\cos\theta). \quad (27)$$

The η_0 thus obtained, together with the higher phase shifts, is recorded in Table II.

We may now use our phase shifts in (27) to compare with Born approximation. In Fig. 4 is shown the differential cross section $|f(q)|^2$, thus calculated, together with its Born equivalent $|u(q)/2\pi|^2$, defined by (9).

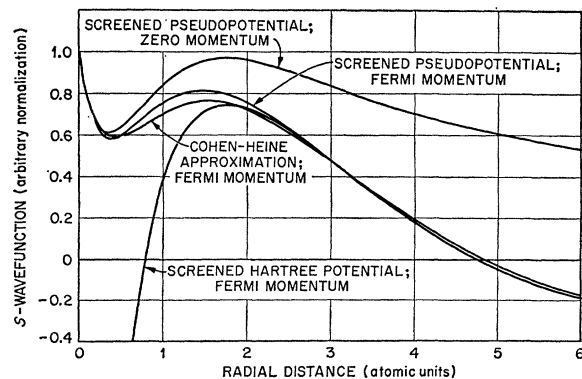


FIG. 3. s -partial-wave solutions of Eqs. (25) and (26). The screened Hartree curve is derived from the screened pseudopotential result using Eq. (5). It extrapolates to give an ordinate of -5.67 at $r=0$.

²¹ Equation (26) was solved iteratively by guessing a $\langle \Psi | U | R_0 \rangle$ and solving the differential equation for an R_0 which then leads to a revised matrix element.

TABLE II. Phase shifts calculated from the Hartree field around a screened lithium ion with 1s orbital parameter α .

α	η_0	η_1	η_2	η_3	η_4
2.69	0.396	0.533	0.047	0.004	0.000
3.00	0.484	0.458	0.043	0.004	0.000

While the curves are qualitatively similar and might be considered in moderate agreement under other circumstances, such is the extreme sensitivity of the curves to back scattering that the Born resistivity of $27.8 \mu\Omega$ cm, calculated in Sec. III, and in reasonable agreement with experiment, is raised to $118 \mu\Omega$ cm.

Let us next draw attention to the final l -dependent potential, which is shown in Fig. 5. That appropriate

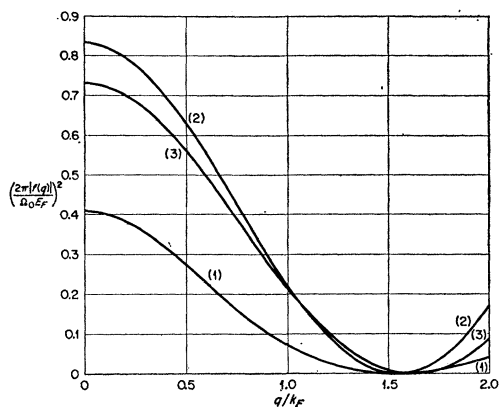


FIG. 4. Various approximations to $|f(q)|^2$, the differential cross section. The symbols Ω_0 and E_F denote, respectively, the specific volume and Fermi energy. Curve (1) represents the Born approximation $2\pi f(q) \sim u(q)$, see Eq. (9), where the core states are as in the free ion ($\alpha=2.69$). Curve (2) shows the result of using phase shifts, still retaining $\alpha=2.69$. Curve (3) shows the reduction brought about by contracting the core to $\alpha=3.00$.

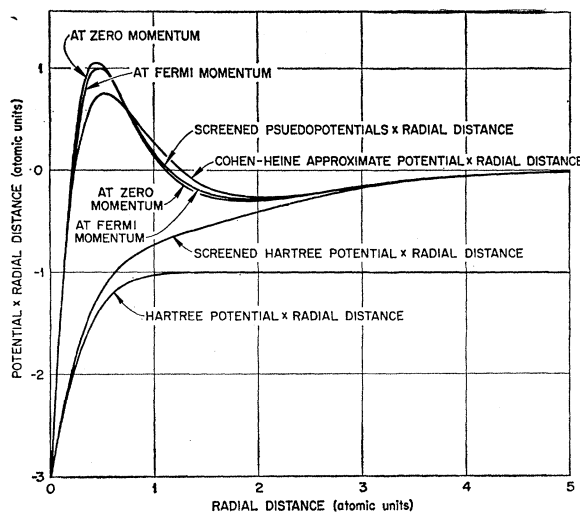
to partial waves not of s type, at any energy, is just the screened Hartree potential $U+U_S$ of Eq. (25). For s waves, we rewrite (26) as

$$[-(1/2r)(d^2/dr^2)r + U + U_S + U_P]R_0 = \mathcal{E}R_0, \quad (28)$$

$$U_P = -\langle \Psi | U | R_0 \rangle \Psi / R_0,$$

and thus obtain an energy-dependent potential. The variation, however, as indicated in Fig. 5, is very small over the energy range $(0, \frac{1}{2}k_F^2)$ and thus, for practical purposes, we have a semilocal potential.⁴ The reason for this energy insensitivity in U_P is that R_0 varies little with energy in the core region, as may be seen in Fig. 3. We have drawn wave functions and potentials together in Fig. 6 to illustrate the response of the various waves to their respective fields.

Cohen and Heine have discussed a method for reducing pseudopotentials to semilocal form. In the present context, this amounts to assuming not only that R_0 is energy-independent, which as we have seen, is enough



Potential x Radial Distance for Liquid Lithium at Melting Point.

FIG. 5. Potentials characterizing a screened lithium ion.

to give a semilocal potential, but also that its value may be taken to be unity in estimating U_P as defined in (28). The general argument hinges on the observation that if the pseudopotential technique were to result in an almost complete cancellation of the potential within the core, R_0 would vary little in that region for energies of interest. In fact, as Figs. 5 and 6 indicate, cancellation is far from complete. Nevertheless, the hump in the potential induces a minimum in the associated s wave around the classical orbital radius α^{-1} . Thus, this wave function is fairly constant in the region where it matters most, and the Cohen-Heine approximation works rather well. Specifically, it gives an s -wave phase shift of 0.346 compared with the previously calculated value of

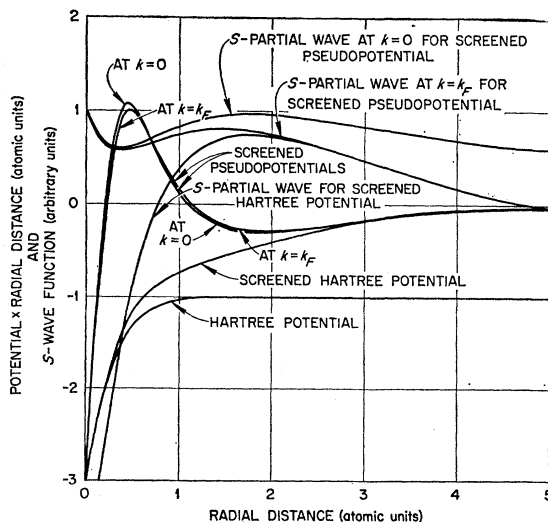


FIG. 6. Response of the s waves to their respective fields.

0.396. Our conclusion is, then, that the Cohen-Heine reduction is better than one might imagine if one were to suppose that success depended on the use of a large number of core orbitals to cancel almost completely the core field.

V. SELF-CONSISTENT SCREENING

It is clear from Sec. IV that we need to reduce the amount of scattering taking place. One mechanism for doing this suggests itself from the evaluated form of U_S shown in Fig. 7, namely, a shrinkage of the core from its free-ion size. We now go on to investigate this matter.

For a satisfactorily self-consistent result with $\alpha=2.69$, we would require U_S to be sensibly constant over the core region. That the calculated U_S is quite flat is an indication that we are very near the optimum situation. But as Fig. 7 shows, the qualitative effect of the valence-electron field is to produce some core shrinkage. This result is a consequence of $U_S(q)$ taking on negative values in the neighborhood of $q=2k_F$ (see Fig. 8). There is no such occurrence in the case of linear dielectric shielding of a simple point-charge potential, say, for it arises from the repulsive core-orthogonality term U_R dominating in (7) in a region beyond $q\sim 1$. (Figure 8 gives also, of course, the potential at large²² as well as at small distances from the nucleus, but detailed consideration of this matter has been deferred.)

It is possible to obtain by perturbation theory²³ some idea of the expected self-consistent α . An estimate of

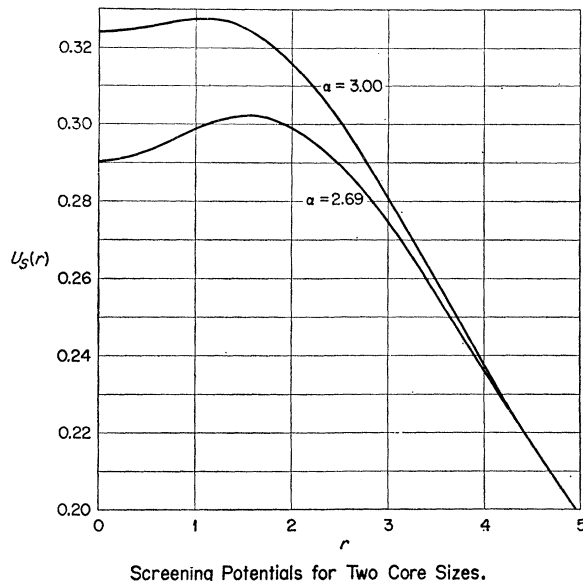
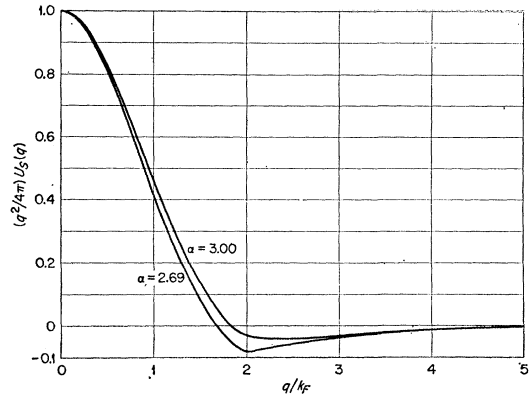


Fig. 7. Screening potentials for two assumed orbital parameters.

²² M. D. Johnson and N. H. March, *Phys. Letters* **3**, 313 (1963); T. Gaskell and N. H. March, *ibid.* **7**, 169 (1963); M. D. Johnson, P. Hutchinson, and N. H. March, *Proc. Roy. Soc. (London)* **A282**, 283 (1964).

²³ W. H. Young and N. H. March, *Phys. Rev.* **109**, 1854 (1958).



Screening Charge Density Fourier Components for Two Core Sizes.

Fig. 8. Fourier components of displaced charge for two assumed orbital parameters. In both cases, the dip to negative values gives rise, at short distances, to a very small contracting force on the core. At large distances, one obtains the usual oscillations.

the first-order Rayleigh-Schrödinger correction to Ψ is $(f - \langle \Psi | f | \Psi \rangle) \Psi$, where

$$f = 2 \int_0^r dr (r\Psi)^{-2} \int_0^r dr (r\Psi)^2 (U_S - \langle \Psi | U_S | \Psi \rangle). \quad (29)$$

On evaluating the perturbed wave function and fitting to an exponential form, we find a revised α of 2.69(2).

One should not attach importance to either the sign or magnitude of the change induced in α as a result of the above calculation, primarily because of such inherent uncertainties as, for example, are present in the choice of pseudopotential and in the linear screening approximation. Nevertheless, because an effect of this kind might have some physical significance, we felt it desirable to see how the differential cross section would change if the core were significantly contracted. Consequently, we repeated our calculations for the arbitrarily chosen case of $\alpha=3.00$, the results being summarized in Table II and Figs. 4, 7, and 8. As expected, the scattering is reduced, but not by a sufficiently large amount (the resistivity, for example, being lowered to $62 \mu\Omega \text{ cm}$).

Now let us consider the Friedel sum rule.²⁴ This tells us, in the present case of lithium, that general considerations of over-all charge neutrality require

$$(2/\pi) \sum (2l+1) \eta_l = 1. \quad (30)$$

Use of Table II shows that the left side of this equation gives 1.44 for $\alpha=2.69$ and 1.34 for $\alpha=3.00$. These results indicate that, even allowing for possible core contraction, the free-electron linear screening approximation is probably deficient, at least for the purpose of calculating the phase shifts.

However, when calculating the form factor, it is known^{6,8} that Born approximation automatically leads

²⁴ J. Friedel, *Phil. Mag.* **43**, 153 (1952).

to a satisfactory result in the forward direction. Thus, even if the screening charge is rather poorly given, Born approximation furnishes a desirable scaling device.

VI. DISCUSSION

In the above work, we investigated, with little approximation of a nonessential kind, the electronic structure of a screened lithium ion, using recently developed pseudopotential techniques. Thus, we have been able to test some of the approximations and assumptions which, perforce, have had to be made hitherto in this area of study. The matters investigated in this way are listed in Sec. I.

On self-consistently applying a linearly screened pseudopotential method to lithium, we find that (i) while the effect of screening on the core-valence exchange operator is small, it is not negligible, (ii) the Slater approximation in the treatment of core-valence exchange is qualitatively incorrect, (iii) the core states are well described by their free-ion forms, (iv) the assumption of a semilocal potential is very good and the Cohen-Heine estimate of it is fairly good, and (v) though the screening charge is considerably overestimated, Born approximation furnishes a desirable scaling of the form factor.

The high degree of accuracy demanded in the differential cross section in order to calculate successfully the electrical resistivity has deeply impressed us. This critical dependence on the electron-ion interaction is in marked contrast with the lattice-vibrational dependence in solids.²⁵ As we have seen, a heavy emphasis is placed on large-angle scattering. This means that even small differences in scattering amplitude in this region are magnified to give large differences in the resistivity. Thus, the usual criteria for the validity of Born approximation may no longer apply, and a phase shift calculation may be necessary. However, our experience shows that it is vitally important to satisfy the Friedel sum rule. Rather than violate this requirement, it is better to use Born approximation, which provides a desirable scaling, by satisfactorily describing the forward scattering.

As noted above, the calculated phase shifts considerably overestimated the displaced charge, and there would appear to be two possible explanations of this. Perhaps the screening is not sufficiently well described by first-order perturbation theory, but that this is masked by the scaling property we have already discussed. If so, this is reminiscent of the recent work of Springer,²⁶ who used the pseudopotential as an expansion parameter and obtained an illusory agreement with experiment in first order. But it could be that we have used a core potential which is too strong. This suggests that we explore the possibility of using more general

orbitals than the choice (2). Because our formalism lends itself to such a generalization, we are considering the possibility of looking into this matter. The results shown in Fig. 7 for two rather different orbital parameters indicate that whatever our final choice of core functions, self-consistency between the valence and bound electrons will be maintained, in the sense that the screening field will exert negligible distorting forces on the core.

Finally, the success of the Cohen-Heine analysis, under rather extreme conditions, is noteworthy. Quite apart from the conceptual simplicity of a semilocal potential, our calculations indicate that Cohen and Heine provide us with a computational technique which should be very practicable in more complicated systems than the present one, where our direct method of solution of the pseudopotential equations might not be feasible.

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APPENDIX

The purpose of this Appendix is to supply details concerning the calculation of various mathematical functions defined in the main text.

(i) Derivation of U , as defined by (3)

By definition, we have

$$U = -\frac{3}{r} + 2 \int \frac{d^3r' \Psi^2(r')}{|\mathbf{r}' - \mathbf{r}|}, \quad (\text{A1})$$

where Ψ is the simple exponential function defined by (2). If we multiply (A1) throughout by $\exp(i\mathbf{q} \cdot \mathbf{r})$, integrate and remember that

$$\int \frac{d^3r' e^{i\mathbf{q} \cdot \mathbf{r}'}}{|\mathbf{r}' - \mathbf{r}|} = \frac{4\pi}{q^2} e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (\text{A2})$$

we find

$$U(q) = -(12\pi/q^2) + (8\pi/q^2) \int d^3r' \Psi^2(r') e^{i\mathbf{q} \cdot \mathbf{r}'}. \quad (\text{A3})$$

On using the standard result

$$\int d^3r e^{-\beta r} e^{i\mathbf{q} \cdot \mathbf{r}} = 8\pi\beta(\beta^2 + q^2)^{-2}, \quad (\text{A4})$$

Eq. (A3) becomes

$$U(q) = -(12\pi/q^2) + (8\pi/q^2)(2\alpha)^4 [(2\alpha)^2 + q^2]^{-2}. \quad (\text{A5})$$

Fourier transformation of the latter now gives (3).

²⁵ A. Meyer, Phys. Rev. **116**, 339 (1959).

²⁶ B. Springer, Phys. Rev. **136**, A115 (1964).

(ii) Evaluation of $U_S(q)$, as defined by (7)

Let us rewrite (7) as

$$U_S(q) = U_{S^0}(q) + U_{S^R}(q), \quad (\text{A6})$$

where U_{S^0} and U_{S^R} are the screening potentials associated with U and U_R (cf. Eq. 21).

Turning first to the calculation of $U_{S^0}(q)$, we note $\langle \mathbf{k} + \mathbf{q} | U | \mathbf{k} \rangle = U(q)$ and the latter is given by (A5). Hence,

$$U_{S^0}(q) = \frac{8\pi}{q^2 \epsilon(q)} \frac{2}{(2\pi)^3} U(q) \int_{k < k_F} d^3k \frac{1}{E_k - E_{k+q}} \\ = U(q) [1/\epsilon(q) - 1], \quad (\text{A7})$$

where the reader is reminded that

$$\epsilon(q) = 1 + \frac{1}{2\pi k_F \eta^2} \left(\frac{1 - \eta^2}{2\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| + 1 \right), \quad \eta = \frac{q}{2k_F}. \quad (\text{A8})$$

To find $U_{S^R}(q)$ is much more trouble. The unscreened matrix element is easily obtained. One notes that

$$\langle \Psi | U | \mathbf{k} \rangle = -4\pi(\alpha^3/\pi)^{1/2} [(\alpha^2 + k^2)^{-1} \\ + 2(9\alpha^2 + k^2)^{-1} + 12\alpha^2(9\alpha^2 + k^2)^{-2}], \quad (\text{A9})$$

and thus

$$\langle \mathbf{k} + \mathbf{q} | U_R | \mathbf{k} \rangle \\ = -\langle \Psi | U | \mathbf{k} \rangle \langle \mathbf{k} + \mathbf{q} | \Psi \rangle \\ = 32\pi\alpha^4(\alpha^2 + |\mathbf{k} + \mathbf{q}|^2)^{-2} [(\alpha^2 + k^2)^{-1} \\ + 2(9\alpha^2 + k^2)^{-1} + 12\alpha^2(9\alpha^2 + k^2)^{-2}], \quad (\text{A10})$$

where (A4) has been used.

In order to calculate

$$U_{S^R}(q) = \frac{8\pi}{q^2 \epsilon(q)} \frac{2}{(2\pi)^3} \int_{k < k_F} d^3k \frac{\langle \mathbf{k} + \mathbf{q} | U_R | \mathbf{k} \rangle}{E_k - E_{k+q}}, \quad (\text{A11})$$

we replace (A10) by

$$\langle \mathbf{k} + \mathbf{q} | U_R | \mathbf{k} \rangle = 32\pi\alpha^4(\alpha^2 + |\mathbf{k} + \mathbf{q}|^2)^{-2} \\ \times [(\alpha^2 + k^2)^{-1} + 10/27\alpha^2]. \quad (\text{A12})$$

It will be noted this is an extremely good approximation for $k < k_F \sim 0.6$ and $\alpha \sim 3$. Thus, after a great deal of labor, (A11) becomes

$$U_{S^R}(q) = \frac{8\pi}{q^2 \epsilon(q)} \frac{2}{(2\pi)^3} \\ \times 32\pi\alpha^4 \left[\int_{k < k_F} d^3k \frac{1}{(\alpha^2 + k^2)(\alpha^2 + |\mathbf{k} + \mathbf{q}|^2)^2 (E_k - E_{k+q})} \right. \\ \left. + \frac{10}{27\alpha^2} \int_{k < k_F} d^3k \frac{1}{(\alpha^2 + |\mathbf{k} + \mathbf{q}|^2)^2 (E_k - E_{k+q})} \right] \\ = -[128\alpha^4/q^3 \epsilon(q)] [F(q) - F(-q)], \quad (\text{A13})$$

in which

$$F(q) = F_1(q) + (10/27\alpha^2)F_2(q), \quad (\text{A14})$$

where

$$F_1(q) = \frac{1}{4}(\alpha^2 + k^2)^{-2} \{ \ln[\alpha^2 + (k+q)^2] - \ln|k + \frac{1}{2}q| \} \\ + (4\alpha^2 + q^2)^{-2} \{ 4 \ln|k + \frac{1}{2}q| - [(8\alpha^2 + q^2)/2\alpha q] \\ \times \tan^{-1}(k/\alpha) - [(4\alpha^2 + 7q^2)/4q^2] \ln[\alpha^2 + (k+q)^2] \\ + [(2\alpha^2 - q^2)/\alpha q] \tan^{-1}[(k+q)/\alpha] \} \\ + [2\alpha q(4\alpha^2 + q^2)]^{-1} \\ \times [k\alpha(\alpha^2 + k^2)^{-1} + \tan^{-1}(k/\alpha)], \quad (\text{A15})$$

and

$$F_2(q) = \frac{1}{2}(\alpha^2 + k^2)^{-1} \{ \ln[\alpha^2 + (k+q)^2] - \ln|k + \frac{1}{2}q| \} \\ - (4\alpha^2 + q^2)^{-1} \{ \ln[\alpha^2 + (k+q)^2] - 2 \ln|k + \frac{1}{2}q| \} \\ - (q/\alpha)(4\alpha^2 + q^2)^{-1} \tan^{-1}[(k+q)/\alpha]. \quad (\text{A16})$$

Equations (A7), (A13), (A14), (A15), and (A16) now explicitly give $U_S(q)$ on substituting in (A6).

(iii) Evaluation, in Dirac form [cf. Eq. (16)], of $A_S(q)$ as defined by (13)

We proceed, much as in part (ii) above, by calculating the two parts exhibited in (21). We begin by evaluating

$$\langle \mathbf{k} + \mathbf{q} | A | \mathbf{k} \rangle = - \int \int \frac{d^3r' d^3r}{|\mathbf{r}' - \mathbf{r}|} \\ \times e^{-i(\mathbf{k} + \mathbf{q}) \cdot \mathbf{r}} \Psi(\mathbf{r}') \Psi(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}'}, \quad (\text{A17})$$

which, on transforming the Coulombic term and using (A4), may be rewritten

$$\langle \mathbf{k} + \mathbf{q} | A | \mathbf{k} \rangle = -(32\alpha^5/\pi) \int d^3K K K^{-2} \\ \times [\alpha^2 + (\mathbf{k} + \mathbf{K} + \mathbf{q})^2]^{-2} [\alpha^2 + (\mathbf{k} + \mathbf{K})^2]^{-2}. \quad (\text{A18})$$

The latter was approximated by writing

$$\langle \mathbf{k} + \mathbf{q} | A | \mathbf{k} \rangle = -(32\alpha^5/\pi) \int d^3K K K^{-2} [\alpha^2 + (\mathbf{K} + \mathbf{q})^2]^{-2} \\ \times (\alpha^2 + K^2)^{-2} \{ 1 - 2[\alpha^2 + (\mathbf{K} + \mathbf{q})^2]^{-1} [2\mathbf{k} \cdot (\mathbf{K} + \mathbf{q}) + k^2] \\ - 2(\alpha^2 + K^2)^{-1} (2\mathbf{k} \cdot \mathbf{K} + k^2) \}. \quad (\text{A19})$$

Note that two expansions were made, both expansion parameters being of the type

$$(\alpha^2 + K^2)^{-1} (2\mathbf{k} \cdot \mathbf{K} + k^2) \\ < 2\{[(2\alpha/k)^2 + 1]^{1/2} - 1\}, \quad (\text{all } \mathbf{K}). \quad (\text{A20})$$

For $k_F \sim 0.6$, $\alpha \sim 3$, the latter can be as high as 0.22 (though only for a limited range of \mathbf{k} and \mathbf{K}). Consequently, we included the first-order terms in the expansion. [On subsequent numerical calculation, the total correction due to such terms never affected $A_{S^0}(q)$ by more than 5% out to $q \sim 3$, when the whole expression

becomes very small in any case.] Use of (A19) now leads to

$$\langle \mathbf{k} + \mathbf{q} | A | \mathbf{k} \rangle = -32\pi\alpha^2(L - M\mathbf{k} \cdot \mathbf{q} - \frac{1}{2}k^2N), \quad (\text{A21})$$

where

$$L = (q^2 + 10\alpha^2)(q^2 + \alpha^2)^{-1}(q^2 + 4\alpha^2)^{-2}, \quad (\text{A22})$$

$$M = \frac{4}{q^3\alpha^3} \tan^{-1}\left(\frac{q\alpha}{q^2 + 2\alpha^2}\right) - 4 \frac{(q^4 + 10q^2\alpha^2 + 32\alpha^4)}{q^2\alpha^2(q^2 + 4\alpha^2)^3} - \frac{(q^2 + 28\alpha^2)}{(q^2 + \alpha^2)(q^2 + 4\alpha^2)^3} + \frac{(5q^4 + 91q^2\alpha^2 + 140\alpha^4)}{(q^2 + \alpha^2)^2(q^2 + 4\alpha^2)^3}, \quad (\text{A23})$$

and

$$N = (3q^6 + 43q^4\alpha^2 + 266q^2\alpha^4 + 280\alpha^6) \times \alpha^{-2}(q^2 + \alpha^2)^{-2}(q^2 + 4\alpha^2)^{-3}. \quad (\text{A24})$$

Thus, we have

$$A_S^0(q) = \frac{8\pi}{q^2\epsilon(q)} \frac{2}{(2\pi)^3} \int_{k < k_F} d^3k \frac{\langle \mathbf{k} + \mathbf{q} | A | \mathbf{k} \rangle}{E_{\mathbf{k}} - E_{\mathbf{k} + \mathbf{q}}} \quad (\text{A25})$$

$$= (128\alpha^2/\epsilon(q))(LP + MQ + NR), \quad (\text{A25})$$

where [recollect (A8)]

$$P = \frac{1}{4}\pi[\epsilon(q) - 1], \quad (\text{A26})$$

$$Q = -q\left\{\frac{1}{3}\eta^{-3} - \frac{1}{2}\pi q[\epsilon(q) - 1]\right\}, \quad (\text{A27})$$

and

$$R = -(q/32)\left[\frac{1}{2}\eta^{-1} + \frac{1}{6}\eta^{-3} + \frac{1}{4}(\eta^{-4} - 1) \times \ln|(1 + \eta)/(1 - \eta)|\right]. \quad (\text{A28})$$

It now remains to calculate $A_S^R(q)$. Once more, we find the unscreened matrix element. To this end, we consider

$$\langle \Psi | A | \mathbf{k} \rangle = - \int \int \frac{d^3r' d^3r}{|\mathbf{r}' - \mathbf{r}|} \Psi^2(r') \Psi(r) e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (\text{A29})$$

The integral over \mathbf{r}' is evaluated using (A1), whence

$$\langle \Psi | A | \mathbf{k} \rangle = -\frac{1}{2}\langle \Psi | U | \mathbf{k} \rangle - \frac{3}{2}\langle \Psi | (1/r) | \mathbf{k} \rangle. \quad (\text{A30})$$

Use of (2) and (3) now gives the expression (23) for

$\langle \Psi | A | \mathbf{k} \rangle$, and thus we explicitly find

$$\langle \Psi | A_R | \mathbf{k} \rangle = -\langle \Psi | A | \mathbf{k} \rangle \langle \mathbf{k} + \mathbf{q} | \Psi \rangle. \quad (\text{A31})$$

In view of the analytic form of (A30), it will be noted that

$$A_S^R(q) = \frac{8\pi}{q^2\epsilon(q)} \frac{2}{(2\pi)^3} \int_{k < k_F} d^3k \frac{\langle \Psi | A_R | \mathbf{k} \rangle}{E_{\mathbf{k}} - E_{\mathbf{k} + \mathbf{q}}} \quad (\text{A32})$$

has, essentially, already been evaluated. From (A10), (A11), (A13), and (A14), we see that

$$A_S^R(q) = -\frac{1}{2}U_S^R(q) - [192\alpha^4/q^3\epsilon(q)][F_1(q) - F_1(-q)]. \quad (\text{A33})$$

(iv) Evaluation, in Slater form [cf. Eq. (17)], of $A_S(q)$ as defined by (13)

The same routine is followed as in (iii); we calculate $A_S^0(q)$ and $A_S^R(q)$ for use in (21). In the present case, we have, using (A4),

$$\langle \mathbf{k} + \mathbf{q} | A | \mathbf{k} \rangle = A(q) = -8\pi ab(b^2 + q^2)^{-2}, \quad (\text{A34})$$

where $a = 3\alpha(3/4\pi^2)^{1/3}$ and $b = \frac{2}{3}\alpha$. Thus, we easily evaluate the screened term from

$$A_S^0(q) = A(q)\{[1/\epsilon(q)] - 1\}. \quad (\text{A35})$$

Now let us consider $A_S^R(q)$. We have

$$\langle \Psi | A | \mathbf{k} \rangle = -8\pi ac(\alpha^3/\pi)^{1/2}(c^2 + k^2)^{-2}, \quad (\text{A36})$$

where $c = (5/3)\alpha$. Thus,

$$\langle \mathbf{k} + \mathbf{q} | A | \mathbf{k} \rangle = -64\pi ac\alpha^4(c^2 + k^2)^{-2} \times [\alpha^2 + (\mathbf{k} + \mathbf{q})^2]^{-2}. \quad (\text{A37})$$

To evaluate

$$A_S^R(q) = \frac{8\pi}{q^2\epsilon(q)} \frac{2}{(2\pi)^3} \int_{k < k_F} d^3k \frac{\langle \mathbf{k} + \mathbf{q} | A | \mathbf{k} \rangle}{E_{\mathbf{k}} - E_{\mathbf{k} + \mathbf{q}}} \quad (\text{A38})$$

one uses (A37) in the approximate form

$$\langle \mathbf{k} + \mathbf{q} | A | \mathbf{k} \rangle = -64\pi ac\alpha^4 c^{-4} [\alpha^2 + (\mathbf{k} + \mathbf{q})^2]^{-2} \quad (\text{A39})$$

which, for $k < k_F \sim 0.6$, $\alpha \sim 3$, amounts to a maximum error of 3%. Once more, the necessary integrals have already been performed [see Eq. (A13)], and we obtain

$$A_S^R(q) = -[256a\alpha^4/c^3q^3\epsilon(q)][F_2(q) - F_2(-q)]. \quad (\text{A40})$$