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New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem*

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A set of successively more accurate self-consistent equations for the one-electron Green's function have been derived. They correspond to an expansion in a screened potential rather than the bare Coulomb potential. The first equation is adequate for many purposes. Each equation follows from the demand that a corresponding expression for the total energy be stationary with respect to variations in the Green's function. The main information to be obtained, besides the total energy, is one-particle-like excitation spectra, i.e., spectra characterized by the quantum numbers of a single particle. This includes the low-excitation spectra in metals as well as configurations in atoms, molecules, and solids with one electron outside or one electron missing from a closed-shell structure. In the latter cases we obtain an approximate description by a modified Hartree-Fock equation involving a "Coulomb hole" and a static screened potential in the exchange term. As an example, spectra of some atoms are discussed. To investigate the convergence of successive approximations for the Green's function, extensive calculations have been made for the electron gas at a range of metallic densities. The results are expressed in terms of quasiparticle energies $E(\mathbf{k})$ and quasiparticle interactions $f(\mathbf{k},\mathbf{k}')$. The very first approximation gives a good value for the magnitude of $E(\mathbf{k})$. To estimate the derivative of $E(\mathbf{k})$ we need both the first- and the second-order terms. The derivative, and thus the specific heat, is found to differ from the free-particle value by only a few percent. Our correction to the specific heat keeps the same sign down to the lowest alkali-metal densities, and is smaller than those obtained recently by Silverstein and by Rice. Our results for the paramagnetic susceptibility are unreliable in the alkali-metal-density region owing to poor convergence of the expansion for f. Besides the proof of a modified Luttinger-Ward-Klein variational principle and a related self-consistency idea, there is not much new in principle in this paper. The emphasis is on the development of a numerically manageable approximation scheme.

1. INTRODUCTION

ONE-PARTICLE equations are widely used to give an approximate description of complicated interacting systems of particles. The Hartree-Fock (HF) equations are used for atoms and molecules, the shell-model equations for nuclei, the Hückel equations for aromatic molecules, and the periodic potential equations for calculation of the energy-band structure of solids. These equations were originally little more than a fairly effective phenomenological model of the system. In the last ten years with the development of formal techniques to treat many-particle systems, much work has been done to connect these equations with an exact theory. Although we now have a wealth of beautiful general theorems, fairly little has been done towards manageable and reliable approximation schemes especially for interacting electrons.

The high-density electron gas is a case that has been examined diligently. Its properties are expressed as series expansions in r_s, where $4\pi r_s^3 a_0^3/3=\Omega/N=1/\rho$, with $a_0=$ Bohr radius $=0.5292\times10^{-8}$ cm. In the metallic density region $r_s=2$-5, most of the series expansions, however, predict manifestly wrong results.

In this paper *the electron-gas problem is reinvestigated, formally and numerically, with the main purpose of estimating the convergence of our expansion in the metallic density region.* The application of the method for solids and particularly for alkali metals will be discussed in another paper.[1]

The results of this paper also provide *a new approach to, and qualitative conclusions regarding, the general type of excitation spectra, which correspond to a single excited electron outside or a hole in a closed-shell structure.* In particular, the alkali atoms and the Born-Heisenberg type of polarization correction are discussed. The treatment is concerned only with a nonrelativistic description of electrons moving in a fixed configuration of nuclei.

In Secs. 2–5 the main results of the formal analysis are presented, detailed derivations being given in the Appendices. In Secs. 6–10 the numerical results for an electron gas are given and the accuracy of our approximations discussed. Section 11 contains a summary of important results.

2. FORMAL FRAMEWORK

The conceptual tool to be used is the one-particle Green's function,[2]

$$G(1,2)=-(i/\hbar)\langle T(\psi(1)\psi^\dagger(2))\rangle. \tag{1}$$

Here 1 and 2 each stand for the five coordinates of a

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.
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[1] L. Hedin, Arkiv. Fysik (to be published).
[2] P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959). See also T. Kato, T. Kobayashi and M. Namiki, Progr. Theor. Phys. Suppl. **15**, 3 (1960); A. Klein, *Lectures on the Many-Body Problem*, edited by E. R. Caianiello (Academic Press Inc., New York, 1962), p. 279; P. Nozières, *The Theory of Interacting Fermi Systems* (W. A. Benjamin, Inc., New York, 1964); A. A. Abrikosov, L. P. Gorkov and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

particle: space, spin, and time, $(1)=(\mathbf{r}_1,\zeta_1,t_1)=(\mathbf{x}_1,t_1)=x_1$. T is the Dyson time-ordering operator and ψ is the field operator in the Heisenberg representation. The brackets stand for averaging with respect to the *exact* ground state, rather than the noninteracting ground state of the system.

The Green's function G obeys the equation

$$[\epsilon-h(\mathbf{x})-V(\mathbf{x})]G(\mathbf{x},\mathbf{x}';\epsilon)-\int M(\mathbf{x},\mathbf{x}'';\epsilon)G(\mathbf{x}'',\mathbf{x}';\epsilon)d(\mathbf{x}'')=\delta(\mathbf{x},\mathbf{x}')\,, \quad (2)$$

where

$$h(\mathbf{x})=-(\hbar^2/2m)\nabla^2-\sum_n^{\text{all nuclei}} Z_n v(\mathbf{x},\mathbf{R}_n)\,,$$

$$V(\mathbf{x})=\int v(\mathbf{x},\mathbf{x}')\rho(\mathbf{x}')d(\mathbf{x}')\,,$$

Z_n and $\mathbf{R}_n$ = charge and position of the nth nucleus,

$$v(\mathbf{x},\mathbf{x}')=e^2/|\mathbf{x}-\mathbf{x}'|\,,$$

$$\rho(\mathbf{x})=\langle\psi^\dagger(\mathbf{x})\psi(\mathbf{x})\rangle$$

$$=\text{number density of the electrons}$$

$$=-i\hbar G(\mathbf{x},t;\mathbf{x},t+\Delta)\,,\quad(\Delta\to 0,\Delta>0)\,,$$

$$G(\mathbf{x},\mathbf{x}';\epsilon)=\int G(\mathbf{x},t;\mathbf{x}',t')\exp\left[\frac{i\epsilon}{\hbar}(t-t')\right]d(t-t')\,.$$

M is the self-energy operator which represents the complicated correlation effects of a many-particle system. A series expansion of M in v gives as first term the HF exchange potential,

$$M^{\mathrm{HF}}(\mathbf{x},\mathbf{x}';\epsilon)=-v(\mathbf{x},\mathbf{x}')\langle\psi^\dagger(\mathbf{x}')\psi(\mathbf{x})\rangle=i\hbar v(\mathbf{x},\mathbf{x}')G(\mathbf{x},t;\mathbf{x}',t+\Delta)\,, \quad (3)$$

which obviously is independent of ϵ.

Later we will write down a set of functionals of G giving successively more accurate approximations of M. Since both V and M are given in terms of G, Eq. (2) represents a self-consistency problem which can also be formulated as a variational problem.

From definition (1) it readily follows that

$$G(\mathbf{x},\mathbf{x}';\epsilon)=\sum_s\left(f_s(\mathbf{x})f_s^*(\mathbf{x}')/(\epsilon-\epsilon_s)\right)\,,$$

where

$$\begin{aligned} f_s(\mathbf{x})&=\langle N,0|\psi(\mathbf{x})|N+1,s\rangle;\\ &\qquad\epsilon_s=E_{N+1,s}-E_{N,0}-i\Delta \quad \text{when } \epsilon_s\geq\mu\,,\\ f_s(\mathbf{x})&=\langle N-1,s|\psi(\mathbf{x})|N,0\rangle;\\ &\qquad\epsilon_s=E_{N,0}-E_{N-1,s}+i\Delta \quad \text{when } \epsilon_s<\mu\,, \end{aligned} \quad (4)$$

and

$$\mu=E_{N+1,0}-E_{N,0}=\text{chemical potential}=-(\text{electron affinity}).$$

$|N,0\rangle$ stands for the ground state of the N-particle system and the sum s runs over *all* states of the $N+1$ and $N-1$ particle systems, the configuration of the nuclei being unchanged.

The amplitudes $f_s(\mathbf{x})$ and the energies ϵ_s are solutions of the eigenvalue equation[3]

$$[\epsilon-h(\mathbf{x})-V(\mathbf{x})]f(\mathbf{x})-\int M(\mathbf{x},\mathbf{x}'';\epsilon)f(\mathbf{x}'')d(\mathbf{x}'')=0\,, \quad (5)$$

in case of a discrete energy value ϵ_s. In the continuous part of the spectrum the solution of (5) in general gives a complex eigenvalue, ϵ. The real part of ϵ represents some average energy of a group of excited states and the imaginary part of ϵ the spread in energy of these states. It is understood that we use the analytical continuation of M into the complex ϵ plane.

The self-consistent solution of Eq. (2) using $M=M^{\mathrm{HF}}$ gives a G built up from the f_s and ϵ_s which are the one-particle functions and energy eigenvalues of the HF approximation. The N smallest values of the ϵ_s correspond to occupied one-electron functions and the remaining to unoccupied or "virtual" functions.

Besides giving information on excitation spectra, the one-particle Green function allows us to calculate the expectation value of any one-particle operator by

$$\langle N|\sum_{i=1}^N 0(\mathbf{x}_i)|N\rangle=\int\langle N|\psi^\dagger(\mathbf{x})0(\mathbf{x})\psi(\mathbf{x})|N\rangle d\mathbf{x}=-i\int\frac{d\epsilon}{2\pi}d(\mathbf{x})e^{i\epsilon\Delta}0(\mathbf{x})G(\mathbf{x},\mathbf{x};\epsilon)\,, \quad (6)$$

and also that of the total-energy operator H by

$$\langle N|H|N\rangle=-i\int\frac{d\epsilon}{2\pi}d(\mathbf{x})d(\mathbf{x}')e^{i\epsilon\Delta}\times\{\delta(\mathbf{x}-\mathbf{x}')(h(\mathbf{x}')+\tfrac{1}{2}V(\mathbf{x}'))+\tfrac{1}{2}M(\mathbf{x},\mathbf{x}';\epsilon)\}\times G(\mathbf{x}',\mathbf{x};\epsilon)+\tfrac{1}{2}\sum_{nm}{}' Z_nZ_m v(\mathbf{R}_n,\mathbf{R}_m)\,. \quad (7)$$

In Eq. (7) the term involving h gives the expectation value of the kinetic energy plus the electrostatic interaction between electrons and nuclei. The term containing V can be written

$$\frac{1}{2}\int\rho(\mathbf{x})v(\mathbf{x},\mathbf{x}')\rho(\mathbf{x}')d\mathbf{x}d\mathbf{x}'\,. \quad (8)$$

---

[3] This equation was first derived, in a very general form, by J. Schwinger, Proc. Natl. Acad. Sci. U. S. **37**, 452 (1951). Its application to many-electron problems has been discussed by G. Pratt, Phys. Rev. **118**, 462 (1960); Rev. Mod. Phys. **35**, 502 (1963); L. Hedin and S. Lundquist, Quantum Chemistry Group, Uppsala, Sweden, Technical Report T III, 1960 (unpublished); L. Hedin, Quantum Chemistry Group, Uppsala, Sweden, Technical Report No. 84, 1962 (unpublished); Bull. Am. Phys. Soc. **8**, 535 (1963).

The MG term gives all exchange and correlation contributions. It is easy to check that Eq. (7) reproduces the HF expression for the energy when G^{HF} and M^{HF} are used.

3. EXPANSION OF M IN TERMS OF A SCREENED POTENTIAL, W

We now turn to our central problem, namely, the development of good approximations for M. The simplest approach is to develop M in a power series of v. It is well known, however, that such an expansion diverges for metals. Even in cases when it is convergent, its convergence rate rapidly becomes poor with increasing polarizability of the system. One common way to handle this problem is to make partial summations to infinite order. The difficulty here is one of knowing what partial summations to choose in order to obtain a systematic theory.

In this paper a new method is developed. We use the Schwinger technique[1] of functional derivatives to generate *an expansion in terms of a screened potential*[4] *W rather than the bare Coulomb potential v.*

The potential W was first introduced by Hubbard[5]:

$$W(1,2)=v(1,2)-\frac{i}{\hbar}\int v(1,3)\langle T(\rho'(3)\rho'(4))\rangle \times v(4,2)d(3)d(4)=W(2,1)\,, \quad (9)$$

where

$$\rho'(1)=\psi^{\dagger}(1)\psi(1)-\langle\psi^{\dagger}(1)\psi(1)\rangle;$$
$$v(1,2)=v(\mathbf{x}_1,\mathbf{x}_2)\delta(t_1-t_2)\,.$$

$W(1,2)$ essentially gives the potential at point 1 due to the presence of a test charge at point 2, including the effect of the polarization of the electrons. W represents the effective interaction between two electrons and is much weaker than the bare Coulomb interaction v if the polarizability is large. W is spin-independent.

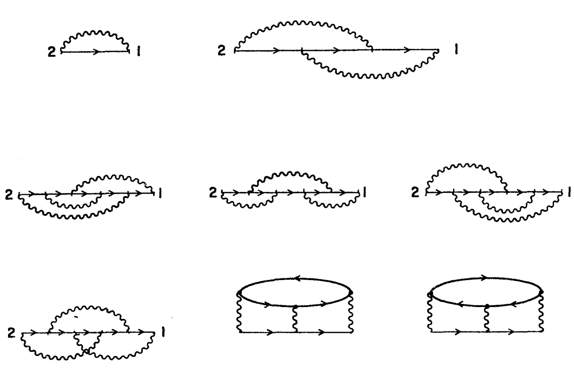

FIG. 1. Diagrams representing the expansion of $M(1,2)$. The one-particle Green's function $G(1,2)$ is represented by an arrow from 2 to 1, and the screened potential $W(1,2)$ by a wiggly line between 1 and 2.

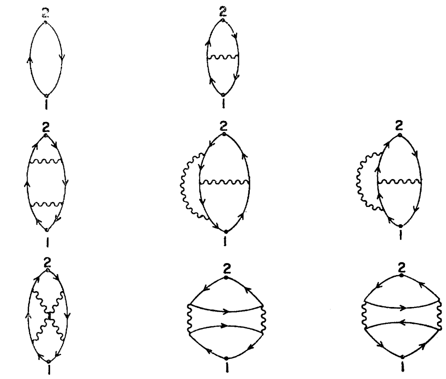

FIG. 2. Diagrams representing the expansion of $P(1,2)$.

The first two terms in the expansion of M are

$$M(1,2)=i\hbar G(1,2)W(1^{+},2)-\hbar^2\int G(1,3)G(3,4) \times G(4,2)W(1,4)W(3,2)d(3)d(4)+\cdots\,, \quad (10)$$

where

$$1^{+}=\mathbf{x}_1,\, t_1+\Delta\,.$$

The expansion for M is represented by diagrams in Fig. 1. There is only one first-order and one second-order term while there are six third-order terms.

The definition (9) of W is not directly useful since it is in terms of the density-density correlation function rather than the Green's function. Instead *we find W from the integral equation*

$$W(1,2)=v(1,2)+\int W(1,3)P(3,4)v(4,2)d(3)d(4)\,, \quad (11)$$

where the kernel P can be expanded as

$$P(1,2)=-i\hbar G(1,2)G(2,1)+\hbar^2\int G(1,3)G(4,1) \times W(3,4)G(2,4)G(3,2)d(3)d(4)+\cdots\,. \quad (12)$$

The expansion for P is represented by diagrams in Fig. 2.

Equations (11) and (12) define W as a functional of G and thus Eq. (10) gives M as a functional of G.[6] G then has to be obtained self-consistently from Eq. (2). The practical usefulness of this scheme of course depends on how many terms in the expansions of M and P are needed to provide a good approximation. In the following we will try to illuminate that question as much as possible.

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[4] The feasibility of expanding in a screened interaction has been emphasized by J. C. Phillips, Phys. Rev. **123**, 420 (1961).

[5] J. Hubbard, Proc. Roy. Soc. **A240**, 539 (1957).

[6] Special cases of such functionals have been proposed by G. Baym and L. P. Kadanoff but no systematic expansion was developed. See G. Baym and L. P. Kadanoff, Phys. Rev. **124**, 287 (1961); G. Baym, Phys. Rev. **127**, 1391 (1962); L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

4. REPRESENTATION OF M BY A "COULOMB HOLE" PLUS SCREENED EXCHANGE

To start with we exhibit the structure of the first-order term in M. From the spectral resolution of G and of the density-density correlation function in W we have

$$M(\mathbf{x},\mathbf{x}';\epsilon)=\int_{-\infty}^{\infty}d\tau\sum_s \exp\left[\frac{i\tau}{\hbar}(\epsilon-\epsilon_s)\right]f_s(\mathbf{x})f_s^*(\mathbf{x}')[\theta(\tau)-\theta(\mu-\epsilon_s)]$$
$$\times\left\{v(\mathbf{x},\mathbf{x}')\delta(\tau+\Delta)-\frac{i}{\hbar}\int v(\mathbf{x},\mathbf{x}'')\sum_t{}' R_t(\mathbf{x}'')R_t^*(\mathbf{x}''')\exp\left(-\frac{i|\tau|}{\hbar}\epsilon_t\right)v(\mathbf{x}''',\mathbf{x}')d\mathbf{x}''d\mathbf{x}'''\right\},\quad(13)$$

$$\theta(\tau)=\begin{matrix}1 & \text{for } \tau>0\\ 0 & \text{for } \tau<0.\end{matrix}$$

The term inside the curly brackets is $W(1^+,2)$. $R_t(\mathbf{x})$ is an oscillator strength function,

$$R_t(\mathbf{x})=\langle N,t|\psi^\dagger(\mathbf{x})\psi(\mathbf{x})|N\rangle,\quad(14)$$

the ordinary oscillator strength being

$$\frac{2m}{\hbar^2}\epsilon_t\left|\int R_t(\mathbf{x})\mathbf{r}\cdot\mathbf{n}\,d\mathbf{x}\right|^2,\quad(15)$$

where $\mathbf{n}$ gives the direction of the dipole moment and $\epsilon_t=E_{N,t}-E_N$. The prime on the sum over t in Eq. (13) indicates that the term with $\epsilon_t=0$ is excluded.

One important use of M is in Eq. (5), which gives the excitation spectra of the $(N\pm1)$-particle systems. The energy shift of a level k caused by M is approximately,

$$\int f_k^*(\mathbf{x})M(\mathbf{x},\mathbf{x}';\epsilon_k)f_k(\mathbf{x}')d\mathbf{x}\,d\mathbf{x}'$$
$$=\int d\tau\sum_s\exp\left[\frac{i\tau}{\hbar}(\epsilon_k-\epsilon_s)\right][\theta(\tau)-\theta(\mu-\epsilon_s)]$$
$$\times\langle ks|W(\tau)|ks\rangle.\quad(16)$$

Here,

$$\langle ks|W(\tau)|ks\rangle=\int f_k^*(\mathbf{x})f_s(\mathbf{x})W(\mathbf{x},\mathbf{x}';\tau)$$
$$\times f_s^*(\mathbf{x}')f_k(\mathbf{x}')d\mathbf{x}\,d\mathbf{x}',\quad(17)$$

is a Coulomb integral when $k=s$, and an exchange integral when $k\neq s$. Generally the Coulomb integral will be much larger than the exchange integrals and the largest exchange integrals will correspond to energies ϵ_s close to ϵ_k. In many cases then the important energy difference, $\epsilon_k-\epsilon_s$, will be small compared to the important energy ϵ_t that appears in W. Assuming that to be the case, we put the factor $\exp[(i\tau/\hbar)(\epsilon-\epsilon_s)]$ in M equal to 1 and obtain,

$$M(\mathbf{x},\mathbf{x}';\epsilon)=\tfrac{1}{2}\delta(\mathbf{x}-\mathbf{x}')W_p(\mathbf{x},\mathbf{x}';0)$$
$$-W(\mathbf{x},\mathbf{x}';0)\langle\psi^\dagger(\mathbf{x}')\psi(\mathbf{x})\rangle.\quad(18)$$

Here $W_p=W-v$ and we have used the fact that

$$\sum_s f_s(\mathbf{x})f_s^*(\mathbf{x}')=\delta(\mathbf{x}-\mathbf{x}');$$
$$\sum_s f_s(\mathbf{x})f_s^*(\mathbf{x}')\theta(\mu-\epsilon_s)=\langle\psi^\dagger(\mathbf{x}')\psi(\mathbf{x})\rangle.\quad(19)$$

The first factor in Eq. (18) gives the contribution of a "*Coulomb hole*"[7] since, according to general results of linear response theory,

$$W_p(\mathbf{x},\mathbf{x}';0)=\int v(\mathbf{x},\mathbf{x}'')\Delta\rho(\mathbf{x}'')d\mathbf{x}''$$
$$=-i\int v(\mathbf{x},\mathbf{x}'')R(\mathbf{x}'',\mathbf{x}''';0)v(\mathbf{x}''',\mathbf{x}')d\mathbf{x}''d\mathbf{x}''',\quad(20)$$

where $\Delta\rho(\mathbf{x}'')$ is the change in number density at the point $\mathbf{x}''$ caused by the presence of a point charge at point $\mathbf{x}'$. $R(\mathbf{x},\mathbf{x}';0)$ is the density-density correlation function. The factor $\frac{1}{2}$ arises mathematically from $\theta(\tau)$ and physically because the force on the electron due to the induced charge is proportional to

$$\mathrm{grad}_{\mathbf{x}}\int v(\mathbf{x},\mathbf{x}'')\Delta\rho(\mathbf{x}'')d\mathbf{x}''=\tfrac{1}{2}\,\mathrm{grad}_{\mathbf{x}}W_p(\mathbf{x},\mathbf{x};0).$$

The last term in Eq. (18) is a *screened exchange* potential. If we replace W by v, the Coulomb hole disappears, the screened exchange potential becomes unscreened and we are back at the HF expression for M. We will abbreviate the "Coulomb hole plus screened exchange" approximation by COHSEX.

For the Rydberg-like spectra of one electron outside a closed shell, the assumptions behind COHSEX are readily verified. Let us take sodium as an example. Here the smallest $(N+1)$-type excitation energy is $\epsilon_1=E(\mathrm{Na},1s^22s^22p^63s)-E(\mathrm{Na}^+,1s^22s^22p^6)=-0.378$ Ry,

[7] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934); E. Wigner, *ibid.* **46**, 1002 (1934); Trans. Faraday Soc. **34**, 678 (1938).

TABLE I. Quasiparticle energies in rydbergs. (Experimental values without reference are taken from Charlotte Moore's tables.)

N		$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	$4p$	$5p$
2	He, HF	−1.8359[a]								
	He, expt	−1.8073								
2	Li^+, HF	−5.5847[a]	−0.3934[b]	−0.2574[b]		−0.11354[b]			−0.06356[b]	−0.04050[b]
	Li^+, expt	−5.5597	−0.3963	−0.2629		−0.11448			−0.06394	−0.04075
10	Ne, HF	−65.5446[c]	−3.8606[a]	−1.7007[a]						
	Ne, expt	−63.89[c]	−3.5628[c]	−1.5874						
10	Na^+, HF	−81.5190[c]	−6.1474[a]	−3.5944[a]	−0.372[d]	−0.2188[d]		−0.1406[d]	−0.1002[d]	
	Na^+, expt	−79.88[c]	−5.8866	−3.4810	−0.3777	−0.2231		−0.1432	−0.1019	
10	Mg^{++}, HF		−8.944[e]	−5.990[e]						
	Mg^{++}, expt		−8.7359	−5.8970						
10	Si^{4+}, HF		−16.17[f]	−12.41[f]	−3.275[f]	−2.639[f]	−1.839[f]	−1.538[f]	−1.319[f]	−0.793[f]
	Si^{4+}, expt		−15.962	−12.273	−3.3180	−2.6655	−1.8565	−1.5502	−1.3279	−0.7977
18	Ar, HF	−237.2202[c]		−19.1426[c]	−2.5545[c]	−1.1818[c]				
	Ar, expt	−234.6[c]		−18.28[c]	−2.1491	−1.1627				
18	K^+, HF	−267.5042[c]		−23.5962[c]	−3.9275[c]	−2.3409[c]				
	K^+, expt	−264.8[c]		−22.63[c]	−3.5288[c]	−2.3387				
18	Ca^{++}, HF				−5.557[g]	−3.756[g]	−0.6659[g]	−0.8295[g]	−0.6193[g]	
	Ca^{++}, expt				−5.1634	−3.7743	−0.7478	−0.8725	−0.6416	
36	Kr, HF							−2.303[h]	−1.06[h]	
	Kr, expt							−2.0386	−1.0453	

[a] P. S. Bagus, T. Gilbert, C. C. J. Roothaan, and H. D. Cohen, (to be published).
[b] V. Fock and M. Petrashen, Physik. Z. Sowjetunion **8**, 547 (1935).
[c] P. S. Bagus, University of Chicago thesis, (to be published).
[d] V. Fock and M. Petrashen, Physik. Z. Sowjetunion **6**, 368 (1934).
[e] W. J. Yost, Phys. Rev. **58**, 557 (1940).
[f] D. R. Hartree, W. Hartree, and M. F. Mannig, Phys. Rev. **60**, 857 (1941).
[g] D. R. Hartree and W. Hartree, Proc. Roy. Soc. **A164**, 167 (1938).
[h] B. H. Worsley, Proc. Roy. Soc. **A247**, 390 (1958).

while the smallest excitation energy appearing in W is

$$E(\mathrm{Na}^+,1s^22s^22p^5(2P_{3/2}{}^0)3s) - E(\mathrm{Na}^+,1s^22s^22p^6)=2.414\text{ Ry}.$$

The average $(\epsilon_1-\epsilon_s)$ will be numerically smaller than ϵ_1 unless the exchange integrals with the continuum and the core states have great influence.

For higher Rydberg-like states the functions f_s are well outside the closed shell. The exchange term then becomes negligible. We can further make a multipole expansion of the two v's in the Coulomb hole term. The result is simply

$$M(\mathbf{x},\mathbf{x}';\epsilon)=-(\alpha e^2/2|\mathbf{r}|^4)\delta(\mathbf{x},\mathbf{x}'), \tag{21}$$

where α is the ion-core polarizability. Eq. (21) was first derived by Born and Heisenberg[8] in 1924. It has been rederived by quantum-mechanical methods,[9] and widely used[10] to obtain polarizabilities from spectral data.

[8] M. Born and W. Heisenberg, Z. Physik **23**, 388 (1924).
[9] I. Waller, Z. Physik **38**, 635 (1926); J. E. Mayer and M. G. Mayer, Phys. Rev. **43**, 605 (1933); J. H. Van Vleck and N. G. Whitelaw, *ibid.* **44**, 551 (1933); H. Bethe, *Handbuch der Physik*, edited by H. Geiger and Karl Scheel (Julius Springer-Verlag, Berlin, 1933), 24.1, 431.
[10] D. R. Bates, Proc. Roy. Soc. **A188**, 350 (1947); E. Trefftz and L. Biermann, Z. Astrophys. **30**, 275 (1952); A. S. Douglas, Proc. Cambridge Phil. Soc. **52**, 687 (1956); K. Bockasten, Arkiv Fysik **10**, 567 (1956) and others.

The Coulomb-hole contribution will lower the energy while screening of the exchange will raise the energy relative to the HF value. *Experimental values of* ϵ_s *are generally lower than the* HF *values for* $\epsilon_s>\mu$ *and higher for* $\epsilon_s<\mu$. To the extent that Eq. (18) remains valid, *this shows that the Coulomb-hole correction dominates for the higher orbitals while the screening of the exchange dominates for the core orbitals.* A comparison between HF values and experimental values is given in Table I.

5. LANDAU FERMI-LIQUID THEORY. THE QUASIPARTICLE INTERACTION IN TERMS OF W

Many important aspects of the theory of metals depend only on the excitation spectrum close to the Fermi surface. This can advantageously be discussed in the framework of Landau's Fermi-liquid theory.[11] For simplicity we here treat only the electron gas in a uniform background of positive charge.

Since the electron gas is translationally invariant, $G(1,2)$ and $M(1,2)$ depend only on the difference between 1 and 2. A Fourier transform with respect to space

[11] L. D. Landau, Zh. Eksperim. i Teor. Fiz. **30**, 1058 (1956); **32**, 59 (1959); **35**, 97 (1958) [English transls.: Soviet Phys.—JETP **3**, 920 (1956); **5**, 101 (1957); **8**, 70 (1959)]. See also P. Nozières, Ref. 2.

and time transforms Eq. (2) into

$$[\epsilon-\epsilon(\mathbf{k})]G(k)-M(k)G(k)=1;\qquad k=(\mathbf{k},\epsilon);\ \epsilon(\mathbf{k})=\hbar^2\mathbf{k}^2/2m.\quad(22)$$

The Fourier transforms are defined as

$$G(k)=\int \exp(i(\mathbf{kr}+\epsilon\tau/\hbar))G(\mathbf{x}_1,t_1;\mathbf{x}_2,t_2)d\mathbf{r}d\tau;\qquad \mathbf{r}=\mathbf{r}_1-\mathbf{r}_2,\quad \tau=t_1-t_2.\quad(23)$$

The set of coordinates k should also contain two spin variables. We omit them since for a paramagnetic ground state, $G(k)$ and $M(k)$ are diagonal in spin with equal diagonal elements. $W(k)$ is spin independent by definition. The V term of Eq. (2) exactly cancels the uniform background of positive charge in the limit of large N.

The expansion for M now becomes

$$M(k)=\frac{i}{(2\pi)^4}\int e^{-i\epsilon'\Delta}W(k')G(k-k')dk'-\frac{1}{(2\pi)^8}\int W(k')W(k'')G(k+k')G(k+k'')G(k+k'+k'')dk'dk''+\cdots;$$
$$W(k)=v(k)/(1-v(k)P(k));\quad v(k)=4\pi e^2/|\mathbf{k}|^2;\quad(24)$$
$$P(k)=-\frac{2i}{(2\pi)^4}\int G(k')G(k'-k)dk'+\frac{2}{(2\pi)^8}\int G(k')G(k'')G(k''-k)G(k'-k)W(k'-k'')dk'dk''+\cdots.$$

The factor 2 in $P(k)$ comes from the spin summation. The eigenvalue equation, Eq. (5), for the quasiparticle energies becomes

$$E(\mathbf{k})=\epsilon(\mathbf{k})+M(\mathbf{k},E(\mathbf{k})).\quad(25)$$

The chemical potential μ is equal to $E(\mathbf{k}_0)$ where $\mathbf{k}_0$, the Fermi momentum, is the same as for the noninteracting gas,[12]

$$|\mathbf{k}_0|=(1/\alpha r_s a_0);\quad \alpha=(4/9\pi)^{1/3}=0.52106.\quad(26)$$

The derivative of $E(\mathbf{k})$ with respect to $|\mathbf{k}|$ at the Fermi surface is

$$E'(\mathbf{k})=\epsilon'(\mathbf{k})+zM'(\mathbf{k},\,\mu+\epsilon(\mathbf{k})-\epsilon(\mathbf{k}_0))$$
$$z^{-1}=1-(\partial M(\mathbf{k}_0,\mu)/\partial\epsilon).\quad(27)$$

Equation (27) was obtained by expanding $M(\mathbf{k},E(\mathbf{k}))$ as

$$M(\mathbf{k},\,\mu+\epsilon(\mathbf{k})-\epsilon(\mathbf{k}_0))+(E(\mathbf{k})-\mu-\epsilon(\mathbf{k})+\epsilon(\mathbf{k}_0))\partial M/\partial\epsilon+\cdots,$$

taking the derivative with respect to $\mathbf{k}$, and solving for $E'(\mathbf{k})$. The prime on M refers to a total derivative, not a partial derivative. Equation (27) is exact on the Fermi surface but only approximate when $|\mathbf{k}|\neq|\mathbf{k}_0|$. $E'(\mathbf{k})$ gives the level density at the Fermi surface and is simply related to the specific heat C[12]:

$$C_0/C=E'(\mathbf{k})/\epsilon'(\mathbf{k}).\quad(28)$$

Here C_0 is the noninteracting or Sommerfeld value of C, $C_0=16.86r_s^2T$ μcal/°K^2 mole. z gives the discontinuity at the Fermi surface in the momentum distribution $n_\sigma(\mathbf{k})=\langle N|a_{\mathbf{k},\sigma}^\dagger a_{\mathbf{k},\sigma}|N\rangle$. Here $a_{\mathbf{k},\sigma}$ is related to the field operator by the relation

$$\psi(\mathbf{x})=(1/\Omega^{1/2})\textstyle\sum_{\mathbf{k},\sigma}a_{\mathbf{k},\sigma}e^{i\mathbf{k}\cdot\mathbf{x}}\chi_\sigma(\zeta).$$

The noninteracting many-particle states of an electron gas are uniquely specified by their momentum distribution $n_\sigma(\mathbf{k})$. Thus, e.g., the paramagnetic ground state is given by

$$n_\sigma^{(0)}(\mathbf{k})=\theta(|\mathbf{k}_0|-|\mathbf{k}|).\quad(29)$$

The basic assumption in Landau's theory of a Fermi liquid is that for small excitation energies there exists a one-to-one correspondence between the noninteracting many-particle states and the true states. It has been proven[13] that the Landau theory is exact to the extent that the interacting many-particle states can be obtained from the noninteracting ones by infinite-order perturbation theory.

The change in energy of the true state corresponding to a change in the distribution function, $n_\sigma(\mathbf{k})=n_\sigma^{(0)}(\mathbf{k})+\delta n_\sigma(\mathbf{k})$, of the noninteracting state is

$$\delta E=\sum_{\mathbf{k},\sigma}E(\mathbf{k})\delta n_\sigma(\mathbf{k})+\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{k}',\sigma,\sigma'}f_{\sigma\sigma'}(\mathbf{k},\mathbf{k}')\delta n_\sigma(\mathbf{k})\delta n_{\sigma'}(\mathbf{k}')+\cdots.\quad(30)$$

Here $E(\mathbf{k})$ is defined by Eq. (25) and f is the quasiparticle interaction. The magnitude of $\mathbf{k}$ and $\mathbf{k}'$ is $|\mathbf{k}_0|$ and f depends only on the angle between them, $f_{\sigma\sigma'}(\theta)$. We split f in two parts,

$$f_{\sigma\sigma'}(\theta)=f_0(\theta)+\delta_{\sigma\sigma'}f_e(\theta).\quad(31)$$

The specific heat and the paramagnetic susceptibilities are obtained from simple integrals involving f. In the former the combination $2f_0+f_e$ enters and in the latter f_e.[11] We can write f as[11]

$$f(\mathbf{k},\mathbf{k}')=2\pi i z_{\mathbf{k}}z_{\mathbf{k}'}\,{}^0\Gamma^0(\mathbf{k},\mathbf{k}'),\quad(32)$$

where ${}^0\Gamma^0$ is defined by the integral equation

[12] J. M. Luttinger, Phys. Rev. **119**, 1153 (1960).

[13] P. Nozières and J. M. Luttinger, Phys. Rev. **127**, 1423, 1431 (1962).

$$^0\Gamma^0(k,k')={}^0I(k,k')+\int {}^0I(k,k'')G^2(k'')\,{}^0\Gamma^0(k'',k')dk'', \quad (33)$$

$$^0I(k,k')=\delta M(k)/\delta G(k').$$

In Eqs. (32) and (33) we have for simplicity taken k to include a spin index. Since M does not contain the Hartree-like potential, ^0I and $^0\Gamma^0$ are the "proper operators" marked with a tilde in Nozières' book.

Using the expansion for M given in Eq. (24) and derived in Appendix A, we obtain the following expansion of f in powers of W

$$f_e(\mathbf{k},\mathbf{k}')=-\frac{z^2}{\Omega}\bigg\{W(\mathbf{k}-\mathbf{k}';0)+\frac{i}{(2\pi)^4}\int[2W(\mathbf{k}-\mathbf{k}';0)W(k'')G(k+k'')G(k'+k'')$$
$$+W(k'')W(k''+k-k')G(k+k'')(G(k'-k'')+G(k+k''))]dk''\bigg\}, \quad (34)$$
$$f_0(\mathbf{k},\mathbf{k}')=\frac{z^2}{\Omega}\frac{i}{(2\pi)^4}\int W^2(k'')G(k+k'')(G(k'-k'')+G(k'+k''))dk''.$$

Here $k=(\mathbf{k},\mu)$ and $k'=(\mathbf{k}',\mu)$. The volume of the system, which appears in the denominator of f, is balanced since the number of terms in the sum in Eq. (30) is of the order of the number of particles. If we indicate the order in W by a superscript, we have that the functional derivative of $M^{(1)}$ gives rise to $f_e^{(1)}$ and $f_0^{(2)}$ while that of $M^{(2)}$ gives the first two terms in $f_e^{(2)}$. The third term in $f_e^{(2)}$ comes from the $^0IG^2\,{}^0\Gamma^0$ term in Eq. (33). The first-order term in f involves only the static screened potential[14,15] and corresponds to the COHSEX approximation (Sec. 4) for M. That approximation for M is however not so clear-cut in the case of an electron gas since the ϵ_t spectrum of W starts at zero rather than at a large finite value. The average value of ϵ_t could, on the other hand, be fairly large since the plasmon energy carries a substantial fraction of the oscillator strength.

From Eq. (18) we find that COHSEX for an electron gas is

$$M(\mathbf{k},\epsilon)=\frac{1}{2}\frac{1}{(2\pi)^3}\int[W(\mathbf{k}',0)-v(\mathbf{k}')]d\mathbf{k}'$$
$$-\frac{1}{(2\pi)^3}\int d\mathbf{k}'\,W(\mathbf{k}',0)\frac{1}{2\pi i}\int e^{i\epsilon'\Delta}G(\mathbf{k}-\mathbf{k}';\epsilon')d\epsilon'. \quad (35)$$

The Coulomb hole term is independent of $\mathbf{k}$ and ϵ and thus a constant. The integration over ϵ' in the last term of Eq. (35) gives, closing the contour in the upper half-plane and using the analytic properties of G,

$$\frac{1}{2\pi i}\int e^{i\epsilon'\Delta}G(\mathbf{k}',\epsilon')d\epsilon'$$
$$=\frac{1}{\pi}\int_{-\infty}^{\mu}\frac{\mathrm{Im}M(\mathbf{k}',\epsilon')d\epsilon'}{[\epsilon'-\epsilon(\mathbf{k}')-\mathrm{Re}M(\mathbf{k}',\epsilon')]^2+[\mathrm{Im}M(\mathbf{k}',\epsilon')]^2}. \quad (36)$$

If we treat ImM as a small energy-independent quantity, the integrand in Eq. (36) becomes a δ function and we obtain for the screened exchange term in Eq. (35),

$$-\frac{1}{(2\pi)^3}\int_{|\mathbf{k}-\mathbf{k}'|<|\mathbf{k}_0|}W(\mathbf{k}',0)\times\left(1-\frac{\partial M[\mathbf{k}-\mathbf{k}',E(\mathbf{k}-\mathbf{k}')]}{\partial\epsilon}\right)^{-1}d\mathbf{k}'. \quad (37)$$

The last factor in Eq. (37) equals z when $|\mathbf{k}-\mathbf{k}'|=|\mathbf{k}_0|$ and it varies fairly slowly with $|\mathbf{k}-\mathbf{k}'|$. Putting this factor equal to z and using Eq. (27), the specific heat comes out the same as from the linear term in f. The magnitude of M is however about 25% too large at metallic densities. Judging COHSEX from what it gives for the magnitude and derivative of $E(\mathbf{k})$ at the Fermi surface, we conclude that it is a rough but reasonable approximation at metallic densities. From our numerical results, to be discussed later in detail, it is clear that COHSEX becomes better the smaller the value of r_s. For small r_s the factor z poses no problem since here[16] $z=1-0.17r_s$ and thus tends to 1.

An approximation similar to that in COHSEX *is useful for estimating higher order diagrams.* The expression for $M^{(1)}$ can be written

$$ihG(1,2)W(1^+,2)=[\langle\psi(1)\psi^\dagger(2)\rangle\theta(\tau)-\langle\psi^\dagger(2)\psi(1)\rangle\theta(-\tau)][v(1^+,2)+W(1^+,2)-v(1^+,2)];$$
$$\tau=t_1-t_2. \quad (38)$$

The approximation in COHSEX consists in neglecting the time-dependence of $\langle\psi\psi^\dagger\rangle$ and $\langle\psi^\dagger\psi\rangle$, or equivalently by replacing

$$W(1^+,2)-v(1^+,2)\to\delta(\tau)[W(1,2)-v(1,2)]_{\epsilon=0}. \quad (39)$$

$M^{(1)}$ is exceptional in the sense that we have to use 1^+ rather than 1 in $W(1,2)$. When this is not the case we

[14] M. Watabe (Ref. 14) has recently treated the Landau theory using this approximation for f. He does not however have the z^2 factor, which is about 0.5 for metallic densities, nor does he take the second-order terms into account.

[15] M. Watabe, Progr. Theoret. Phys. (Kyoto) **29**, 519 (1963).

[16] E. Daniel and S. H. Vosko, Phys. Rev. **120**, 2041 (1960).

can make an approximation in the same spirit as that of COHSEX simply by replacing $W(\tau)$ by $\delta(\tau)W(\epsilon=0)$, or if we work with energy-variables, *by replacing* $W(\epsilon)$ *by* $W(0)$.

It should be noted that while the energy dependence of the M operator is very important for an electron gas (see Sec. 9), it is quite negligible for the alkali atoms discussed earlier. Thus if we have an error $\Delta\epsilon$ in the energy argument of M, the correction is only of the order

$$\Delta\epsilon[M(\epsilon)-M^{\rm HF}]/(\epsilon_t,\text{ average}). \qquad (40)$$

This is easily seen by noting that $M^{\rm HF}$ is energy-independent and that the energy derivative of $[M(\epsilon)-M^{\rm HF}]$ effectively introduces a factor $(\epsilon_t,\text{ average})^{-1}$.

6. ELECTRON GAS: SURVEY OF NUMERICAL RESULTS

So far the discussion has been mainly qualitative. We will now see to what extent it is supported by numerical results for the electron gas. Calculations have been made for $r_s=1$, 2, 3, 4, 5, and 6 and in a few cases for smaller and larger r_s values. *For G we have used the expression*

$$G(\mathbf{k},\epsilon)=1/(\epsilon-\epsilon(\mathbf{k})-\epsilon_0);$$
$$\epsilon(\mathbf{k})=(\hbar^2\mathbf{k}^2/2m)+i\Delta\,\mathrm{sgn}(|\mathbf{k}_0|-|\mathbf{k}|), \qquad (41)$$

where ϵ_0 is chosen so that $\mu=\epsilon(\mathbf{k}_0)+\epsilon_0$. From Eq. (24) we see that if the M operator is $M(\mathbf{k},\epsilon)$ using (41) with $\epsilon_0=0$, it becomes $M(\mathbf{k},\,\epsilon-\epsilon_0)$ for $\epsilon_0\neq0$. P is independent of ϵ_0. The equation for μ is $\mu=\epsilon(\mathbf{k}_0)+M(\mathbf{k}_0,\,\mu-\epsilon_0)$ which combined with the above expression for μ gives,

$$\epsilon_0=M[\mathbf{k}_0,\epsilon(\mathbf{k}_0)]. \qquad (42)$$

It would have been desirable to have used a self-consistent G,

$$G(\mathbf{k},\epsilon)=1/(\epsilon-\epsilon(\mathbf{k})-M(\mathbf{k},\epsilon)). \qquad (43)$$

This should be possible to do but the size of the numerical enterprise is probably considerably larger than is justified in a first investigation. That (41) is not too bad is shown by the fact that $M(\mathbf{k},\epsilon(\mathbf{k}))$ is found to have a very weak $\mathbf{k}$ dependence compared to $\epsilon(\mathbf{k})$. On the other hand $\partial M(\mathbf{k},\epsilon)/\partial\epsilon$ is found to have an appreciable magnitude compared to 1. This might very well effect our quantitative results but can do little to change our qualitative conclusions regarding the convergence of the expansion in W and the smallness of the specific-heat correction.

For M we use the approximation iGW, and for P, the approximation $-iGG$. A quite reliable estimate of the error in the magnitude of M is obtained from a consideration of the total energy of the electron gas. The magnitude of the second-order term in M is also estimated and found to be of the same order as the error in the first-order term.

From the relation $G=G_0+G_0(M-\epsilon_0)G$ we see that the correction to $M^{(1)}=iGW$ from the use of G_0 instead of G is approximately $iG_0(M-\epsilon_0)G_0W=iG_0MG_0W+\epsilon_0\partial M^{(1)}/\partial\epsilon$. This term is appreciably smaller than the uncrossed second-order term appearing in an expansion with $\epsilon_0=0$. The cancellations mentioned by DuBois[51] (p. 54 in his paper) involving this term are discussed in Sec. 9.

The first-order term in the quasiparticle interaction f is trivial. The second-order terms have been calculated using $W(\mathbf{k},0)$. The contribution to the specific heat coming from f_0 has been evaluated with $W(\mathbf{k},\epsilon)$. It is found that the $W(\mathbf{k},0)$ approximation gives about 70% of the $W(\mathbf{k},\epsilon)$ approximation at metallic densities. We assume that the error is about the same for the other second-order term in f. The first-order term in f is about three times larger than the second-order terms for $r_s=4$, the ratio being more favorable for smaller r_s. *The picture of M that emerges shows a quite large first-order term with a weak* $\mathbf{k}$ *dependence and a small second-order term with a k dependence of about the same magnitude and opposite sign.*[17,18]

7. ELECTRON GAS: COULOMB HOLE AND CORRELATION HOLE

For the polarization propagator $P(1,2)$ we have used the approximation $-i\hbar G(1,2)G(2,1)$ with G defined by Eq. (41). This gives Lindhard's expression,[19] or as it is often called, the Random Phase Approximation (RPA) for the dielectric constant. To exhibit the properties of this approximation we investigate the Coulomb and correlation holes associated with P.

We define a propagating dielectric function by the relation

$$W(1,2)=\int v(1,3)\epsilon^{-1}(3,2)d(3). \qquad (44)$$

From Eqs. (9) and (11) it follows that

$$\epsilon^{-1}(1,2)=\delta(1,2)-\frac{i}{\hbar}\int\langle T(\rho'(1)\rho'(3))\rangle \times v(3,2)d(3)=(1-Pv)^{-1}(1,2). \qquad (45)$$

The function ϵ^{-1} is closely related to the linear response function ϵ_L^{-1},

$$\epsilon_L^{-1}(1,2)=\delta(1,2)-\frac{i}{\hbar}\theta(t_1-t_2) \times\int\langle[\rho(1),\rho(3)]\rangle v(3,2)d(3), \qquad (46)$$

[17] Recent calculations by Rice (Ref. 18) indicate that the energy dependence of W is more important for the first term in $f_e^{(2)}$, Eq. (34), than for the other second-order terms in f. While this makes the convergence properties of the expansion for f worse than anticipated from our results, it does not influence the conclusion regarding a weak $\boldsymbol{k}$ dependence of M. Our values for the paramagnetic susceptibility on the other hand seem quite unreliable.

[18] T. M. Rice, Ann. Phys. (N. Y.) **31**, 100 (1965).

[19] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **28**, No. 8 (1954); D. F. DuBois, Ann. Phys. (N. Y.) **7**, 174 (1959); **8**, 24 (1959).

which gives the change in the density of the electrons,

$$\rho^{\mathrm{ind}}(1)=\int[\epsilon_L^{-1}(1,2)-\delta(1,2)]\rho^{\mathrm{ext}}(2)d(2)\,,\qquad(47)$$

caused by the presence of an external charge density, ρ^{ext}. The Fourier transforms, $\int\exp[(i\epsilon/\hbar)(t_1-t_2)]dt_1$, of $\epsilon^{-1}(1,2)$ and $\epsilon_L^{-1}(1,2)$ are equal for $\epsilon\gtrless0$. The former is an even function of ϵ, while in the latter the real part is even and the imaginary part odd.

From a knowledge of ϵ^{-1} we can calculate the pair correlation function:

$$g(\mathbf{r})=\rho^{-2}\sum_{ij}{}'\,\langle\delta(\mathbf{r}_i-\mathbf{r})\delta(\mathbf{r}_j)\rangle=\rho^{-2}[\langle\rho(\mathbf{r})\rho(\mathbf{0})\rangle-\rho\delta(\mathbf{r})]\,,\qquad(48)$$

where

$$\rho(\mathbf{r})=\int\psi^\dagger(\mathbf{r},\zeta)\psi(\mathbf{r},\zeta)d\zeta\,,\quad\rho=\langle\rho(\mathbf{r})\rangle\,.\qquad(49)$$

From the definition of $g(\mathbf{r})$ it readily follows that

$$g(\mathbf{r})\to1\quad\text{when}\quad\mathbf{r}\to\infty$$
$$\int\rho(g(\mathbf{r})-1)d\mathbf{r}=-1\,.\qquad(50)$$

The Fourier transform of $g(\mathbf{r})$ is related to $\epsilon(\mathbf{k},\epsilon)$ by

$$g(\mathbf{k})=\rho^{-2}\left\{\frac{1}{2\pi i}\frac{1}{v(\mathbf{k})}\int[1-\epsilon^{-1}(\mathbf{k},\epsilon)]d\epsilon-\rho\right\}+(2\pi)^3\delta(\mathbf{k})\,.\qquad(51)$$

From $\epsilon(\mathbf{k},\epsilon)$ we can also calculate the linear response value for the change in the electron density around a fixed external point charge. From Eq. (47) we have, taking the external charge to be $-e$ and using the fact that $\epsilon^{-1}(\mathbf{k},0)=\epsilon_L^{-1}(\mathbf{k},0)$,

$$g_0(\mathbf{r})=\int[\epsilon^{-1}(1,2)-\delta(1,2)]dt_1\,d\zeta_1;\quad\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2\,.\qquad(52)$$

The Fourier transform of $g_0(\mathbf{r})$ is

$$g_0(\mathbf{k})=\epsilon^{-1}(\mathbf{k},0)-1\,.\qquad(53)$$

The function $g_0(\mathbf{r})$ gives the *Coulomb hole* discussed in Secs. 4 and 5, while $\rho(g(\mathbf{r})-1)$ gives the *correlation hole* surrounding an electron. From a well-correlated wave function for an atom, the correlation hole can be calculated fairly simply from Eq. (48), while the Coulomb hole requires calculations of the type needed to obtain polarizabilities.

We note that *the Coulomb holes for an electron gas and for a system with an energy gap are qualitatively different.* From Eqs. (46) and (52) we have for a system with an energy gap

$$\int g_0(\mathbf{r})d\mathbf{r}=0\,.\qquad(54)$$

For an electron gas, on the other hand, we have from Eq. (53)

$$\int g_0(\mathbf{r})d\mathbf{r}=g_0(\mathbf{k}=0)=-1\,.\qquad(55)$$

This relation should hold also for metals.[20]

The Lindhard expression[19] for the dielectric constant is

$$\begin{aligned}&\epsilon(\mathbf{k},\epsilon)=1-v(\mathbf{k})P(\mathbf{k},\epsilon)=1+\alpha(\mathbf{k},\epsilon)\,,\\&\alpha(q,u)=(\alpha r_s/8\pi)(1/q^3)[H(q+(u/q))+H(q-(u/q))]=\alpha(q,-u)\,,\\&H(z)=2z+(1-z^2)\ln((z+1)/(z-1))=-H(-z)\,,\\&q=(k/2k_0)\,,\quad u=\epsilon(4\hbar^2k_0^2/2m)^{-1}\,,\\&\alpha=(4/9\pi)^{1/3}=0.52106\,.\end{aligned}\qquad(56)$$

The logarithm is taken from the branch where $|\mathrm{Im}\ln z|<\pi$. To obtain ϵ we have to take $\mathrm{Im}u=\Delta\,\mathrm{sgn}(\mathrm{Re}u)$ while ϵ_L is obtained by taking $\mathrm{Im}u=\Delta$. For further reference we note that

$$\begin{aligned}&H(z)=4\left(\frac{1}{3z}+\frac{1}{15z^3}+\frac{1}{35z^5}+\cdots\right);\quad z\to\infty\,,\\&H(z)=4\left(z-\frac{z^3}{3}-\frac{z^5}{15}-\frac{z^7}{35}-\cdots\right)-\pi i(1-z^2)\,\mathrm{sgn}(\mathrm{Im}z);\quad z\to0\,,\\&\alpha(q,0)=(\alpha r_s/\pi)1/q^2\,,\quad q\to0;\\&\alpha(q,0)=(\alpha r_s/3\pi)1/q^4\,,\quad q\to\infty\,;\\&\alpha(0,u)=-(\alpha r_s/3\pi)1/u^2\,;\\&\alpha(q,u)=(\alpha r_s/3\pi)1/(q^4-u^2)\,.\quad|q\pm(u/q)|\to\infty\,;\\&\alpha(q,0)>0\quad\text{for all }q;\\&\alpha(q,iu)=\frac{\alpha r_s}{4\pi q^2}\left[2+\frac{w^2+1-q^2}{2q}\ln\frac{w^2+(1+q)^2}{w^2+(1-q)^2}-2w\left(\arctan\frac{1+q}{w}+\arctan\frac{1-q}{w}\right)\right],\quad w=u/q\,.\end{aligned}\qquad(57)$$

The pair correlation function $g(r)$ has been calculated from the RPA expression for $\epsilon^{-1}(q,u)$, $[1+\alpha(q,u)]^{-1}$, and from the HF expression, $1-\alpha(q,u)$ and plotted in Fig. 3. The HF expression is obtained by using a HF wave function in Eq. (45). Both the RPA and the HF

[20] It is possible that Eq. (54) will remain valid if surface effects are taken into account. The corresponding contribution to M however tends to zero with increasing number of particles.

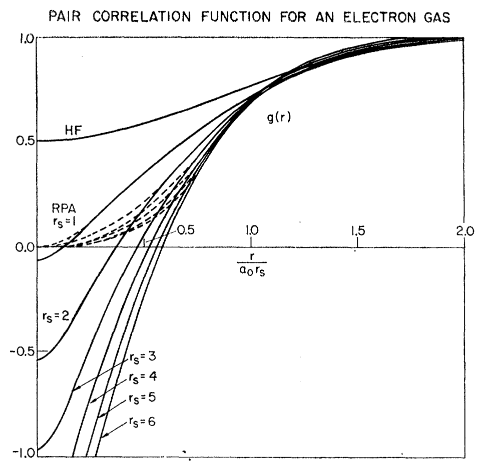

FIG. 3. Pair correlation function for an electron gas.

approximations obey Eq. (50). Since $g(r)$ is a probability it must always be positive but from Fig. 3 we see that the RPA approximation becomes negative[21,22] for small r. In our calculations however we are not directly interested in $g(r)$ but rather in $r^2g(r)$. In Fig. 4 we see that *the influence of the misbehavior of $g(r)$ for small r is suppressed to a large extent by the factor r^2.*

Ueda[23] has calculated $g(r)$ for $r_s=0.1$, 0.5, and 1 using the approximation

$$\epsilon\equiv(1-Pv)^{-1}=(1-P_0v)^{-1}+P_1v\,, \tag{58}$$

where P_0 is the RPA approximation and P_1 is the next term in the expansion Eq. (12) for P, evaluated with G and W from the RPA approximation. For $r=0$ Eq. (58) gives simply

$$g(0)=0.5+0.5[g^{\mathrm{RPA}}(0)-0.5]\,, \tag{59}$$

e.g. it gives one half of the RPA correction to HF. Ueda's approximation changes $g(0)$ for $r_s=1$ and 2 from the RPA values -0.07 and -0.54 to 0.22[24] and -0.02 and thus Ueda's expression also gives a negative $g(0)$ at metallic densities.

While Eq. (58) is a good approximation for the small values of r_s that Ueda considered, for metallic densities one should rather use

$$\epsilon^{-1}=(1-P_0v)^{-1}+(1-P_0v)^{-1}P_1v(1-P_0v)^{-1}. \tag{60}$$

This expression however can be expected to give an even smaller correction to RPA than does Ueda's. To improve significantly upon RPA it is thus not enough to take $P=P_0+P_1$ with a simple RPA approximation for G and W.

Considering $P(\mathbf{k},\epsilon)$ in the limit of small $\mathbf{k}$, Glick,[25] reached the conclusion that one has to take the infinite

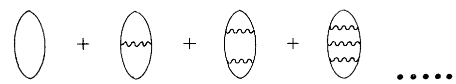

FIG. 5. The ladder-bubble diagrams of Eq. (61).

sum of ladder-bubble diagrams,

$$P=\text{diagrams of Fig. 5}\,, \tag{61}$$

in order to keep $\mathrm{Im}\epsilon(\mathbf{k},\epsilon)$ positive for all ϵ. Starting from Ward identities Engelsberg and Schrieffer[26] and Lundqvist[27] also arrived at Eq. (61) in the cases of electron-phonon and electron-electron interactions, respectively. *In Appendices A and B we will argue that the ladder-bubble sum does not give a systematic improvement as far as M and G are concerned.* While for the lower metallic densities some infinite summation for P has to be made, for the higher densities it seems more important to explore self-consistent solutions for G to first or perhaps second order in W.

The Coulomb hole $g_0(r)$ has been calculated by Langer and Vosko,[28] with the RPA expression for $\epsilon(q,u)$. The function $g_0(r)$ is qualitatively similar to $\rho(g(r)-1)$. It extends over a distance of order r_sa_0, obeys Eq. (55) and is finite for $r=0$. The magnitude of $g_0(0)$ is however much larger than ρ, and $g_0(0)$ ranges from -2.20ρ for $r_s=1.5$ to -6.35ρ for $r_s=6$. RPA thus predicts that more charge is pushed away, close to the external charge $-e$, than was present at the beginning. This feature

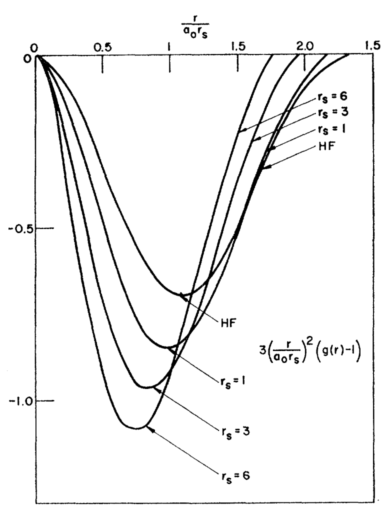

FIG. 4. $3(r/a_0r_s)^2\times[g(r)-1]$. $g(r)$ is the pair correlation function. The area under each curve is equal to -1.

[21] A. J. Glick and R. A. Ferrell (Ref. 21) have calculated the RPA approximation of $g(r)$ for $r_s=2$. They find that $g(0)=-0.15$ while the present calculation gives -0.54. The quantity $g(0)$ can be written $1-c\int_0^\infty k^2f(k)dk$. The reason that their value is in error might be that they fitted $f(k)$ by a Gaussian which underestimates the asymptotic contributions to the integral.

[22] A. J. Glick and R. A. Ferrell, Ann. Physics **11**, 359 (1960).

[23] S. Ueda, Progr. Theoret. Phys. (Kyoto) **26**, 45 (1961).

[24] Ueda reports a slightly different value, 0.19.

[25] A. J. Glick, Phys. Rev. **129**, 1399 (1963).

[26] S. Engelsberg and J. R. Schrieffer, Phys. Rev. **131**, 993 (1963).

[27] B. Lundqvist, (unpublished note from Chalmers' University of Technology, Gothenburg, Sweden).

[28] J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids **12**, 196 (1959).

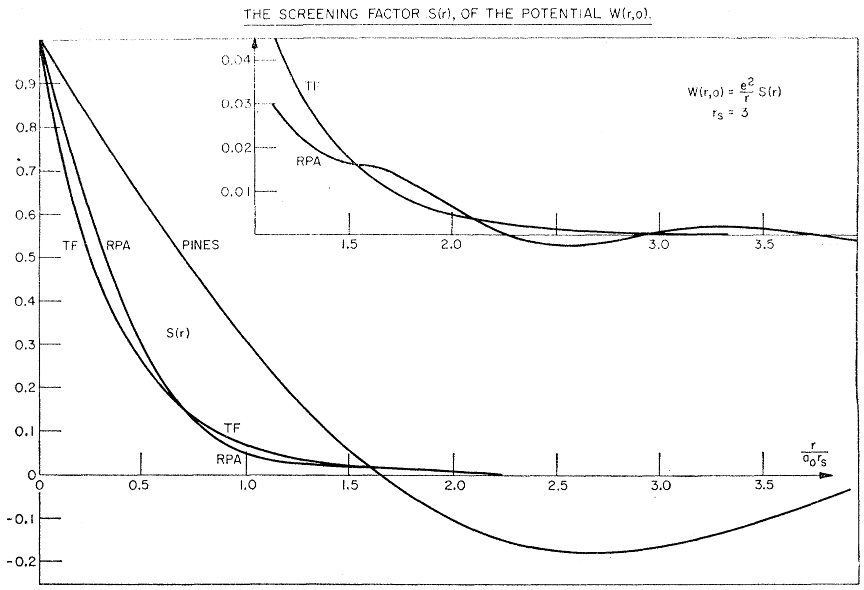

FIG. 6. The screening factor $S(r)$ of the potential $W(r,0)$. $S(r)$ is defined by $W(r,0)=(e^2/r)S(r)$. The curves correspond to $r_s=3$. The Thomas-Fermi (TF) approximation is $S(r)=e^{-k_c r}$, where $k_c=0.815 r_s^{1/2}k_0$. The Pines' expression (Ref. 30) is given in Eq. (63).

might be true also for the correct $g_0(r)$ since it is defined from a linear response expression.

The behavior of $g_0(r)$ for small r has however relatively small influence on $W(r,0)=(e^2/r)S(r)$,

$$S(r)=-4\pi\int_r^\infty r'(r'-r)g_0(r')dr', \tag{62}$$

as can be seen in Fig. 6 where the Thomas-Fermi (TF) and the RPA results[29,30] for $S(r)$ are plotted for $r_s=3$. The TF g_0 tends to infinity for small r but still the TF S threads the RPA S quite well. As a comparison we have also plotted Pines' expression,[31]

$$S(r)=1-(2/\pi)Si(x),\quad x=k_c r,\quad k_c=0.353 r_s^{1/2}k_0,$$
$$Si(x)=\int_0^x \frac{\sin t}{t}dt, \tag{63}$$

which is quite different from the two others.

The HF expression for ϵ, namely, $\epsilon^{-1}(q,u)=1-\alpha(q,u)$, gives a reasonable result for $r=0$:

$$g_0(0)=-\tfrac{3}{2}\pi\alpha r_s\rho, \tag{64}$$

but predicts a completely wrong asymptotic behavior,

$$g_0(r)=-3\alpha^2 r_s(a_0 r_s/r)\rho;\quad r\to\infty, \tag{65}$$

which makes the integral in Eq. (55) divergent.

[29] $S(r)$ has also been calculated by March and Murray (Ref. 30) by a rather complicated method. The results for $S(r)$ as obtained from Langer and Vosko's densities (Ref. 28) using Eq. (62) agree within 0.1% with those of March and Murray's for $r_s=1.5$. Other r_s values cannot be accurately checked since they lie far from those used by Langer and Vosko.

[30] N. H. March and A. M. Murray, Proc. Roy. Soc. **A261**, 119 (1961).

[31] D. Pines, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 387.

8. ELECTRON GAS: THE TOTAL ENERGY

Our primary interest in this paper is to calculate the electron self energy M. By considering the total energy we can obtain an estimate of the error in $\mu=(\hbar^2\mathbf{k}_0^2/2m)+M(\mathbf{k}_0,\mu)$. The relations between ϵ, the energy per particle, and μ are[32]

$$\mu=\epsilon-\tfrac{1}{3}r_s(d\epsilon/dr_s),$$
$$\epsilon=3r_s^3\int_{r_s}^\infty \frac{\mu(x)}{x^4}dx. \tag{66}$$

The curve $\epsilon(r_s)$ has its minimum in the neighborhood of $r_s=4$ and here an error in ϵ gives essentially the same error in μ.

To calculate $\epsilon(r_s)$ we use the virial theorem for an electron gas[33]:

$$V+2T+r_s(d\epsilon/dr_s)=0, \tag{67}$$

where V and T are the expectation values of the potential and kinetic energies divided by the number of particles. Solving Eq. (67), we have, considering V to be expressed in rydbergs,

$$\epsilon=\frac{1}{r_s^2}\left[A+\int_0^{r_s} xV(x)dx\right]\text{Ry}. \tag{68}$$

From the known behavior[34] of ϵ for small r_s we infer that the integration constant A is

$$A=3/5\alpha^2=2.2099. \tag{69}$$

[32] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 343; J. J. Quinn and R. A. Ferrell, Phys. Rev. **112**, 812 (1958).

[33] N. H. March, Phys. Rev. **110**, 604 (1958).

[34] M. Gell-Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957).

For convenience we write $V(r_s)$ as

$$V(r_s)=(1/r_s)(V_{\mathrm{corr}}-B)$$
$$B=3/2\pi\alpha=0.9163\,, \tag{70}$$

which allows us to express the correlation energy $\epsilon_c=\epsilon-\epsilon^{\mathrm{HF}}$ as

$$\epsilon_c=\frac{1}{r_s^2}\int_0^{r_s}V_{\mathrm{corr}}(x)dx\ \mathrm{Ry}\,. \tag{71}$$

V_{corr} can be calculated from the dielectric constant[35] $1+\alpha(q,u)$:

$$V_{\mathrm{corr}}=\frac{4}{\pi\alpha}\int_0^\infty dq\left(\frac{6}{\alpha r_s}\int_0^\infty du\frac{q^2\alpha(q,iu)}{1+\alpha(q,iu)}-1\right)+B\,, \tag{72}$$

which, when we use the RPA expression for $\alpha(q,u)$, becomes

$$V_{\mathrm{corr}}=-\frac{24}{\pi\alpha^2r_s}\int_0^\infty dq\int_0^\infty du\frac{q^2\alpha^2(q,iu)}{1+\alpha(q,iu)}\,. \tag{73}$$

From a general theorem given by Ferrell[36] we can deduce a restriction on V_{corr}. Ferrell proved that

$$\partial^2\epsilon/\partial(e^2)^2\leqslant 0 \text{ at constant density,} \tag{74}$$

where e is the electron charge. From the relation $\alpha(\hbar^2/m)(3\pi^2\rho)^{1/3}r_s=e^2$, we see that r_s is proportional to e^2 when the density is kept constant. The factor $1/r_s^2$ Ry $=(1/r_s^2)(me^4/2\hbar^2)$ in Eq. (68) then becomes independent of e^2 and the Ferrell condition, Eq. (74), can be written

$$\frac{d^2}{dr_s^2}\left\{A+\int_0^{r_s}[V_{\mathrm{corr}}(x)-B]dx\right\}=\frac{d}{dr_s}V_{\mathrm{corr}}(r_s)\leqslant 0\,. \tag{75}$$

In Fig. 7 we have plotted different expressions for V_{corr}. The series expansion in r_s is taken from Carr and Maradudin[37]:

$$\epsilon_c=0.0622\ln r_s-0.096+0.018r_s\ln r_s-0.036r_s\,,$$
$$V_{\mathrm{corr}}=d(r_s^2\epsilon_c)/dr_s=r_s(0.1244\ln r_s-0.130+0.054r_s\ln r_s-0.090r_s)\,. \tag{76}$$

This V_{corr} violates Eq. (75) from $r_s\approx 2$. The RPA expression for V_{corr} satisfies Eq. (75) at least up to $r_s=100$. The contribution to ϵ_c from exchange of second order in v has been calculated by Gell-Mann and Brueckner.[34] They obtain the value 0.046 Ry which gives a contribution of $0.092r_s$ to V_{corr}. When this is added to RPA, the Ferrell condition becomes violated from $r_s\approx 3$ (see Fig. 7). *The unscreened second-order exchange terms actually represent a substantial overcorrection to* RPA *already at* $r_s=1$, as can be seen by comparing with the r_s expansion.

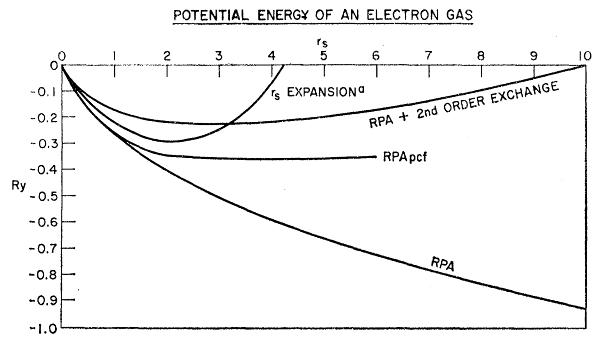

FIG. 7. Potential energy of an electron gas. The quantity $r_s\langle V\rangle+0.9163$ Ry plotted as a function of r_s. The derivative of this quantity is always negative according to a theorem by R. A. Ferrell (Ref. 35). The correlation energy is obtained by an integration,

$$\epsilon_c=\frac{1}{r_s^2}\int_0^{r_s}(r_s\langle V\rangle+0.9163)dr_s\ \mathrm{Ry}.$$

See also Ref. 37.

V_{corr} can also be calculated from the pair correlation function $g(r)$,

$$V_{\mathrm{corr}}=\frac{1}{3\pi\alpha}\int_0^\infty x[g^{\mathrm{RPA}}(x)-g^{\mathrm{HF}}(x)]dx;\quad x=2k_0r\,. \tag{77}$$

As a check on the numerical accuracy of g^{RPA}, Eq. (77) was evaluated and found to give the same result as Eq. (73) within a few percent. Since the $g^{\mathrm{RPA}}(r)$ curves violate the condition $g^{\mathrm{RPA}}>0$, for small r, they were smoothly extrapolated to zero (dashed curves in Fig. 3). *These extrapolated curves were then used in Eq. (77) and the result plotted in Fig. 7 with the label* RPA_{pcf}. Since the correct g lies above g^{RPA} for small r it has to lie below g^{RPA} for some regions of r in order to satisfy the normalization condition. If the correct g were zero for $r=0$ the $\mathrm{RPA}_{pcf}V_{\mathrm{corr}}$ would give a rough upper bound to the correct V_{corr}. At metallic densities the dashed curves in Fig. 3 lie so much above the g^{RPA} curves that a further small shift will make relatively little change in V_{corr}. We conclude that, at metallic densities, the $\mathrm{RPA}_{pcf}V_{\mathrm{corr}}$ is a rough upper bound to the correct V_{corr}.

In Fig. 8 the total energy is plotted as calculated from Eq. (71) using the values for V_{corr} given in Fig. 7. For comparison the HF energy and the energy of the Wigner-type electron lattice[38] are also plotted. We note that while the extrapolation of the g curves looks drastic, the difference between the RPA and the RPA_{pcf} curves for the total energy is fairly small even though the energy calculation involves $rg(r)$ and not $r^2g(r)$, cf. Fig. 4 and the discussion of the correlation hole in Sec. 7.

The phase transition where the electrons cease to be

[35] P. Nozières and D. Pines, Nuovo Cimento **9**, 470 (1958).
[36] R. A. Ferrell, Phys. Rev. Letters **1**, 443 (1958).
[37] W. J. Carr, Jr. and A. A. Maradudin, Phys. Rev. **A133**, 371 (1964).
[38] W. J. Carr, Jr., R. A. Coldwell-Horsfall, and A. E. Fein, Phys. Rev. **124**, 747 (1961).

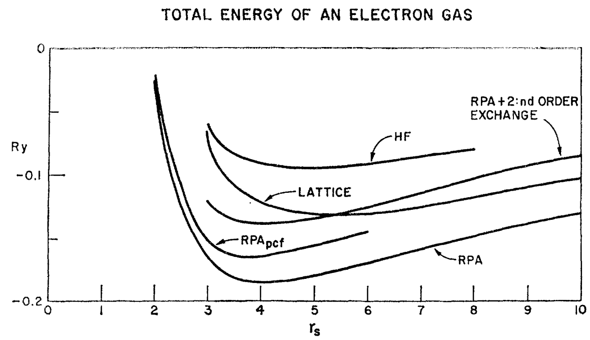

FIG. 8. Total energy of an electron gas. The energy of the electron lattice is taken from Ref. 38.

itinerant and form a lattice has been estimated by de Wette[39] to occur between $r_s \approx 47$ and $r_s \approx 100$. From a calculation to finite order in W we expect to find a smooth energy curve, which, if carried to high enough order in W, will cross the energy curve corresponding to electrons on a Wigner lattice. The RPA curve for the total energy lies below the lattice curve at least up to $r_s = 100$. This gives additional evidence, besides the fact that the second-order term in ϵ is positive, that RPA gives a lower bound to the energy. It is indeed hard to imagine that any reasonable curve for V_{corr} which starts out as the series expansion, has a negative slope, and never goes below -0.876 Ry, could lie lower than the RPA curve. The limit -0.876 Ry is set by the fact that the lattice energy goes asymptotically as $-1.792/r_s$ and the HF energy as $-0.916/r_s$.

If we extrapolate the RPA$_{pcf}$ curve for V_{corr}, Fig. 7, with a horizontal line starting at the minimum, the corresponding curve for the total energy will cross the lattice curve at $r_s \approx 11$. This gives further evidence that the RPA$_{pcf}$ curve is an upper bound to the energy. The RPA$_{pcf}$ total energy actually comes quite close to the results of a calculation by Gaskell.[40] His curve lies 0.003 Ry above and 0.007 Ry below the RPA$_{pcf}$ curve at $r_s = 3$ and $r_s = 5$, respectively. Gaskell made a variational calculation with an antisymmetrized product of pair functions, but due to an additional approximation his results do not quite give a rigorous upper bound for the energy. From all evidence taken together we estimate that *the error in the* RPA *approximation for the energy* ϵ *is positive and at most 0.02* Ry.

We now return to the question of estimating the error in the chemical potential μ. Equation (66) relates the exact ϵ to the exact μ and within the numerical accuracy of our calculations, ± 0.0005 Ry, it holds also for ϵ calculated from Eq. (71) and μ calculated from $M = iGW[P = -iGG$, G according to Eq. (41)]. If for the error in the energy $\Delta\epsilon$, we use the difference between RPA$_{pcf}$ and RPA, we find that the term $\frac{1}{3} r_s d\Delta\epsilon / dr_s$ is small compared to $\Delta\epsilon$ at metallic densities.

[39] F. W. de Wette, Phys. Rev. **135**, A287 (1964).
[40] T. Gaskell, Proc. Phys. Soc. **77**, 1182 (1961); **80**, 1091 (1962).

We estimate that *the error in the* RPA *approximation for the chemical potential* μ *is positive and at most 0.02* Ry.

To further investigate the convergence properties of the expansion for M, Eq. (24), we consider the second-order term. While the first-order term is given by a four-dimensional integral, which easily can be reduced to a two-dimensional integral, the second-order term is given by an eight-dimensional integral which is difficult to reduce to less than a seven-dimensional one. As we discussed in Sec. 5, a rough value can however be obtained by using the static potential $W(\mathbf{k},0)$ instead of the full potential $W(\mathbf{k},\epsilon)$. The second-order term then becomes

$$M^{(2)}(k,u) = \frac{1}{\pi^4} \int \frac{d\mathbf{k}_1 d\mathbf{k}_2}{\mathbf{k}_1{}^2 \mathbf{k}_2{}^2 \epsilon(\mathbf{k}_1,0)\epsilon(\mathbf{k}_2,0)(k^2 - u - 2\mathbf{k}_1 \cdot \mathbf{k}_2)} \text{ Ry}, \quad (78)$$

where the integral is taken over the regions

$$\begin{array}{ccc} |\mathbf{k}+\mathbf{k}_1| \leqslant 0.5 & & |\mathbf{k}+\mathbf{k}_1| \geqslant 0.5 \\ |\mathbf{k}+\mathbf{k}_2| \leqslant 0.5 & \text{and} & |\mathbf{k}+\mathbf{k}_2| \geqslant 0.5 \\ |\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2| \geqslant 0.5 & & |\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2| \leqslant 0.5, \end{array}$$

and the $\mathbf{k}$'s are expressed in units of twice the Fermi momentum and u in units of $(4\hbar^2 k_0{}^2/2m)$. One angular integration is trivial but there still remains a five-dimensional integral. For the particular case of $k=0$, $u=0$, Eq. (78) can however be reduced to a double integral,

$$M^{(2)}(0,0) = \frac{8}{\pi^2} \int \frac{dk_1 dk_2 \operatorname{sgn}(k_1 - 0.5)}{\epsilon(k_1,0)\epsilon(k_2,0) k_1 k_2} \times \ln \left| \frac{2k_1 k_2}{0.25 - k_1{}^2 - k_2{}^2} \right| \text{ Ry}, \quad (79)$$

over the regions

$$0 \leqslant k_1 - k_2 \leqslant 0.5, \quad \text{and} \quad k_1 + k_2 \geqslant 0.5.$$

This integral was evaluated using a TF dielectric constant:

$$\epsilon(k,0) = 1 + (\alpha r_s/\pi)(1/k^2), \quad (80)$$

which is good enough for the present discussion. $M^{(2)}(0,0)$ *was found to vary slowly with* r_s *at metallic densities, reaching a maximum of 0.014* Ry *at* $r_s \approx 3$. From values of $(d/dk) M^{(2)}(k,(\hbar^2 k^2/2m))_{k=k_0}$, Sec. 10, we estimate that $\mu^{(2)} = M^{(2)}(k_0,(\hbar^2 k_0{}^2/2m))$ is about 0.02–0.04 Ry i.e. of about the same size as the error in the first-order contribution $\mu^{(1)}$. It should be realized that while the preceding discussion suggests a very good convergence of the expansion of μ in terms of W, an accurate value of μ cannot be obtained by just adding $\mu^{(2)}$ to μ^{RPA} since the $\mu^{(1)}$ which corresponds to a self consistent solution for G might well differ from μ^{RPA} by an amount comparable to $\mu^{(2)}$.

In the calculation of the energy we have assumed that

TABLE II. Energies of an electron gas in rydbergs.

T_0 = Kinetic Energy in the HF approx. $= (3/5\alpha^2 r_s^2)$ Ry $= (2.2099/r_s^2)$ Ry.

ϵ_{exch} = Potential Energy in the HF approx. $= -(3/2\pi\alpha r_s)$ Ry $= -(0.9163/r_s)$ Ry.

$\epsilon_{\mathrm{corr}}^{\mathrm{RPA}}$ = Correlation energy in the RPA = Total energy − HF energy.

$\epsilon_{\mathrm{corr}}^{\mathrm{a}} = 0.0622 \ln r_s - 0.096 + 0.018 r_s \ln r_s - 0.036 r_s$.

T = Expectation value of the kinetic energy in the RPA.

V = Expectation value of the potential energy in the RPA.

ϵ = Total energy in the RPA $= T+V = T_0 + \epsilon_{\mathrm{exch}} + \epsilon_{\mathrm{corr}}^{\mathrm{RPA}}$.

ϵ_{Ferr} = Total energy of the Ferro-magnetic state according to RPA.

$\epsilon_{\mathrm{Latt}}^{\mathrm{b}}$ = Energy of the Wigner type lattice of electrons

$$= -\frac{1.792}{r_s} + \frac{2.65}{r_s^{3/2}} - \frac{0.73}{r_s^2} + \left(\frac{21}{r_s} - \frac{4.8}{r_s^{3/4}} - \frac{1.16}{r_s^{5/4}}\right) e^{-2.06 r_s^{1/2}} - \left(\frac{2.06}{r_s^{5/4}} - \frac{0.66}{r_s^{7/4}}\right) e^{-1.55 r_s^{1/2}}.$$

The energies are accurate to ±0.0005 Ry.

r_s	T_0	ϵ_{exch}	$\epsilon_{\mathrm{corr}}^{\mathrm{RPA}}$	$\epsilon_{\mathrm{corr}}^{\mathrm{a}}$	T	V	ϵ	ϵ_{Ferr}	$\epsilon_{\mathrm{Latt}}^{\mathrm{b}}$
1	2.2099	−0.9163	−0.1578	−0.132	2.3161	−1.1803	1.1358	2.2502	1.49
2	0.5525	−0.4582	−0.1238	−0.100	0.6299	−0.6594	−0.0295	0.2150	0.173
3	0.2455	−0.3054	−0.1058	−0.076	0.3083	−0.4740	−0.1657	−0.0695	−0.067
4	0.1381	−0.2291	−0.0938	−0.054	0.1920	−0.3767	−0.1847	−0.1367	−0.122
5	0.0884	−0.1833	−0.0851	−0.031	0.1359	−0.3158	−0.1799	−0.1526	−0.131
6	0.0614	−0.1527	−0.0784	−0.007	0.1040	−0.2737	−0.1697	−0.1534	−0.130
7	0.0451	−0.1309	−0.0730	+0.018	0.0839	−0.2427	−0.1588	−0.1482	−0.128
8	0.0345	−0.1145	−0.0685		0.0703	−0.2188	−0.1485	−0.1413	−0.118
9	0.0273	−0.1018	−0.0647		0.0606	−0.1998	−0.1392	−0.1344	−0.110
10	0.0221	−0.0916	−0.0615		0.0532	−0.1842	−0.1310	−0.1274	−0.103

[a] W. J. Carr, Jr., and A. A. Maradudin, Phys. Rev. **133**, A371 (1964).
[b] W. J. Carr, Jr., R. A. Coldwell-Horsfall, and A. E. Fein, Phys. Rev. **124**, 747 (1961).

the ground state is paramagnetic. To obtain the energy of the ferromagnetic state we have to use a Green's function which is zero for, say, spin down and for spin up has a Fermi momentum[41]

$$k_0^F = \beta k_0; \quad \beta = 2^{1/3}; \quad k_0 = (\alpha a_0 r_s)^{-1}. \tag{81}$$

As is well known the HF expression for the energy of the ferromagnetic state is, in Rydbergs,

$$\epsilon^F = \beta^2 (3/5\alpha^2 r_s^2) - \beta (3/2\pi\alpha r_s), \tag{82}$$

which lies below the energy of the paramagnetic state for $r_s \geqslant 5.45$. In RPA we have the simple relation for the correlation energy

$$\epsilon_c^F(r_s) = \tfrac{1}{2}\epsilon_c^P(r_s\beta^{-4}). \tag{83}$$

To see that we introduce dimensionless variables as in Eq. (56) but with k_0 replaced by k_0^F. From Eq. (24) we then find for the dielectric constant

$$\epsilon^F(q,u;r_s) = \epsilon^P(q,u;r_s\beta^{-4}), \tag{84}$$

and from Eq. (73)

$$V_{\mathrm{corr}}^F(r_s) = \beta V_{\mathrm{corr}}^P(r_s\beta^{-4}). \tag{85}$$

Substituting Eq. (85) into Eq. (71) finally gives Eq. (83). We note that Eq. (84) is not valid if we include higher terms in $P(\mathbf{k},\epsilon)$, Eq. (24), or if we use a self-consistent G.

Table II gives the values of the energy for the ferromagnetic state in the RPA as obtained from Eqs. (82) and (83). We see that ϵ^F lies above ϵ^P (given under the heading ϵ in Table II) and approaches it asymptotically. At $r_s = 10$ the difference between the energies is only 3% of their magnitude. This is a reasonable result since the influence of spin orientation has to vanish when the density tends to zero. The present results do not quite rule out the possibility that the electron gas should become ferromagnetic at some density since we know that the RPA value for $\epsilon^P(r_s)$ lies too low. On the other hand, $\epsilon^F(r_s)$ is also too low but perhaps less so since according to Eq. (83) the error in ϵ_c^F is only half the error in ϵ_c^P. It seems safe to predict that *the electron gas does not become ferromagnetic for* $r_s < 7$.

The numbers in Table II not discussed so far are self explanatory. We only note that the series expansion for ϵ_{corr} rapidly becomes bad for $r_s > 3$ and that our values for $\epsilon_{\mathrm{corr}}^{\mathrm{RPA}}$ do not quite coincide with Hubbard's, his values[42] being between 0.002 and 0.004 Ry higher than ours.

9. ELECTRON GAS: THE M OPERATOR

The M operator was calculated from the equation

$$M(\mathbf{k},\epsilon) = \frac{i}{(2\pi)^4}\int \frac{v(\mathbf{k}')d\mathbf{k}'}{\epsilon(\mathbf{k}',\epsilon')} \frac{e^{-i\Delta\epsilon'}d\epsilon'}{\epsilon-\epsilon'-\epsilon(\mathbf{k}-\mathbf{k}')}, \tag{86}$$

cf. Eqs. (24), (41), and (56). The contour for ϵ' runs just below the real axis for $\epsilon' < 0$ and just above for $\epsilon' > 0$.

[41] Superscript $F(P)$ here refers to the ferromagnetic (paramagnetic) state.

[42] J. Hubbard, Proc. Roy. Soc. **A243**, 336 (1957).

We first separate out the HF term:

$$W(\mathbf{k},\epsilon)e^{-i\epsilon\Delta}=\frac{v(\mathbf{k})}{\epsilon(\mathbf{k},\epsilon)}e^{-i\epsilon\Delta}$$
$$=v(\mathbf{k})e^{-i\epsilon\Delta}+v(\mathbf{k})\left(\frac{1}{\epsilon(\mathbf{k},\epsilon)}-1\right). \quad (87)$$

Since, according to Eq. (57), $(1/\epsilon(q,u))-1$ tends to zero as $|u|^{-2}$ for large $|u|$, the convergence factor $e^{-i\epsilon\Delta}$ has been omitted in the last term of Eq. (87). We then separate out the static approximation of the last term in Eq. (87), cf. Sec. 5,

$$W(\mathbf{k},\epsilon)e^{-i\epsilon\Delta}=v(\mathbf{k})e^{-i\epsilon\Delta}$$
$$+v(\mathbf{k})\left(\frac{1}{\epsilon(\mathbf{k},0)}-1\right)+v(\mathbf{k})\left(\frac{1}{\epsilon(\mathbf{k},\epsilon)}-\frac{1}{\epsilon(\mathbf{k},0)}\right). \quad (88)$$

The contributions to $M(q,u)$ from the first two terms of Eq. (88) are easily evaluated by closing the contour for ϵ' in Eq. (86) in the lower half-plane, giving the Coulomb hole plus screened exchange terms,

$$M^c=\frac{4}{\pi\alpha r_s}\int_0^\infty\left(\frac{1}{\epsilon(q',0)}-1\right)dq'$$
$$-\frac{4}{\pi\alpha r_s}\int_{-1}^{1}d\xi\int_0^\infty dq'\frac{\theta(0.25-q^2-q'^2-2qq'\xi)}{\epsilon(q',0)}\,\text{Ry}. \quad (89)$$

To evaluate the contribution from the last term of Eq. (88) we follow Quinn and Ferrell[43] and turn the contour of ϵ' in Eq. (86) to run along the imaginary axis. We pick up a contribution from the poles of the Green's function,

$$M^p=\frac{4}{\pi\alpha r_s}\int_{-1}^{1}d\xi\int_0^\infty dq'\left(\frac{1}{\epsilon(q',\,u-\epsilon(\mathbf{q}-\mathbf{q}'))}-\frac{1}{\epsilon(q',0)}\right)$$
$$\times[\theta(u-\epsilon(\mathbf{q}-\mathbf{q}'))-\theta(0.25-\epsilon(\mathbf{q}-\mathbf{q}'))]\,\text{Ry};$$
$$\xi=\mathbf{q}\cdot\mathbf{q}'/(qq'), \quad (90)$$

as well as the contribution from integrating ϵ' along the imaginary axis,

$$M^r=\frac{1}{\pi^2\alpha r_s}\int_0^\infty du'\int_0^\infty dq'\left(\frac{1}{\epsilon(q',iu')}-\frac{1}{\epsilon(q',0)}\right)$$
$$\times\frac{1}{qq'}\ln\frac{(u-(q+q')^2)^2+u'^2}{(u-(q-q')^2)^2+u'^2}\,\text{Ry}. \quad (91)$$

We thus have

$$M(q,u)=M^c(q)+M^p(q,u)+M^r(q,u). \quad (92)$$

[43] J. J. Quinn and R. A. Ferrell, Phys. Rev. **112**, 812 (1958).

TABLE III. The Fermi energy for an electron gas, $T+M$, in rydbergs.

r_s	T	M^{HF}	M^{RPA}	M^{a}	M^{b}	M^{c}
1	3.6832	−1.2218	−1.3965	−1.8327	−0.4541	−1.6267
2	0.9208	−0.6109	−0.7491	−0.9164	−0.1639	−0.9137
3	0.4092	−0.4073	−0.5259	−0.6110	−0.0870	−0.6577
4	0.2302	−0.3054	−0.4112	−0.4581	−0.0546	−0.5224
5	0.1473	−0.2444	−0.3406	−0.3666	−0.0377	−0.4375
6	0.1023	−0.2036	−0.2926	−0.3054	−0.0277	−0.3787
7	0.0752	−0.1745	−0.2575	−0.2618	−0.0212	−0.3354
8	0.0576	−0.1527	−0.2308	−0.2291	−0.0168	−0.3019
9	0.0455	−0.1358	−0.2097	−0.2037	−0.0136	−0.2753
10	0.0368	−0.1222	−0.1925	−0.1833	−0.0113	−0.2535

[a] The Slater approximation $=1.5\,M^{\mathrm{HF}}$.
[b] Screened exchange potential.
[c] Screened exchange potential plus Coulomb hole contribution.

M^c and M^r are real and the imaginary part of M comes solely from M^p. For $u=0.25$ ($\epsilon=\hbar^2k_0^2/2m$), M^p is zero as well as its first derivatives with respect to q and u. The real part of $M^p(q,q^2)$ is small. It decreases monotonically from about 0.01 Ry at $q=0$ to 0 at $q=0.5$, except for $r_s=1$ when it has a maximum of 0.02 Ry at $q=0.2$. The imaginary part of $M^p(q,q^2)$ is larger as can be seen from Table IV under the heading M_2. It decreases monotonically from values of the order 0.1 Ry at $q=0$ to zero at $q=0.5$. The derivatives of $\mathrm{Re}M^p(q,u)$ with respect to u are 10% or less of the derivative of $M(q,u)$ for $0.5\geqslant q\geqslant 0.2$, but increase rapidly for smaller q.

The first term in $M^c(q)$, the Coulomb hole contribution, is independent of q. The second term in $M^c(q)$, the screened exchange contribution, is substantially smaller than the HF exchange term as can be seen from Table III. Comparing M^c with M^{RPA} in Table III, we can see that M^c has too large a magnitude and that the Slater approximation,[44] which consists of an average of M^{HF} over the Fermi sphere, actually is better.

M^r can conveniently be split into three parts. The first part consists of contributions from integrating u' between 0 and 0.25 in Eq. (91). The second and third parts come from the integration over $u'>0.25$ and the following division:

$$\frac{1}{\epsilon(q',iu')}-\frac{1}{\epsilon(q',0)}=\left(\frac{1}{\epsilon(q',iu')}-1\right)+\left(1-\frac{1}{\epsilon(q',0)}\right). \quad (93)$$

In the third part, i.e., the second term of Eq. (93), the integration over u' can be made analytically,

$$M^{rm}(q,u)=\frac{1}{2\pi^2\alpha r_s}\int_0^\infty dq'\left(1-\frac{1}{\epsilon(q',0)}\right)$$
$$\times\frac{1}{qq'}\left(a\arctan(a)-b\arctan(b)-\tfrac{1}{2}\ln\frac{1+a^2}{1+b^2}\right)\text{Ry};$$
$$a=4((q+q')^2-u),\quad b=4((q-q')^2-u). \quad (94)$$

[44] J. C. Slater, Phys. Rev. **81**, 385 (1951).

M^{rm} gives the main part of M^r, being about three times as large as each of the first two parts with respect both to magnitude and derivatives. The essential contribution to the first part of M^r comes from $q'<0.8$, and to the second part from $q'<2.4$, $u'<3$, the remaining contributions being small and practically independent of q, u, and r_s.

M^c is easily evaluated since the integration over ξ in Eq. (89) can be made analytically. In evaluating M^r we have the advantage that $\epsilon(q,iu)$ is much more well behaved than $\epsilon(q,u)$. From Eq. (57) we see that $\alpha(q,iu)$ only has three singular points, $u=0$, $q=0$, ±1, while $\alpha(q,u)$ is singular along the lines $(q\pm(u/q))=\pm1$. The evaluation of M^p involves $\alpha(q,u)$ but fortunately M^p is small and the relative accuracy does not have to be pushed so far.

The integrals were evaluated for

$$q=0, \qquad u=\pm0.01;$$
$$q=0.1, 0.2, 0.3, 0.4, \quad u=q^2,(q+0.1)^2;$$
$$q=0.5, 0.6, 0.7, \qquad u=q^2,(q-0.1)^2.$$

The results are given in Table IV. The values of M for $u\neq q^2$ are not given directly but in the form

$$z^{-1}(q)=1-\Delta M/\Delta\epsilon. \tag{95}$$

For $q=0$ we have given the average of the results for $u=\pm0.01$. To estimate how well z approximates the limit when $\Delta\epsilon\to0$, we compare the values of $\mathrm{Re}z^{-1}$ for $q=0.4$, 0.5, and 0.6. They agree to about two decimal places which, in conjunction with the fact that $M(q,q^2)$ is almost linear for these q values, shows that $M(q,u)$ *can be represented fairly well by a linear expression in* q *and* u *for* $|q-0.5|<0.1$ *and* $|u-0.25|<0.1$, unless the $M(q,u)$ surface has an anomalous behavior for $u<q^2$, $q<0.5$ and $u>q^2$, $q\geqslant0.5$. To check $\mathrm{Im}z^{-1}$ we note that for u close to 0.25 we have from general arguments[12]

$$M_2(q,u)=C_q(u-0.25)^2\,\mathrm{sgn}(0.25-u). \tag{96}$$

The values of C_q for $q=0.4$ and 0.6 deviate by about 20% from those for $q=0.5$. We can also check Z at $q=0$ where the calculations were made for three values of u. The values of $\mathrm{Im}z^{-1}$ agree within a few percent while the values for $\mathrm{Re}(z^{-1}-1)$ deviate from their mean value by 20%, 29% and 65% at $r_s=1$, 4, and 6, respectively. We conclude that $M_1(0,u)$ *varies very rapidly with* u and that our value for $\mathrm{Re}z^{-1}$ is not very reliable when q is small.

To solve Dyson's equation for the quasiparticle energies we expand

$$\epsilon=\epsilon(\mathbf{k})+M(\mathbf{k},\,\epsilon-\epsilon_0)=\epsilon(\mathbf{k})+M(\mathbf{k},\epsilon(\mathbf{k}))+(\epsilon-\epsilon_0-\epsilon(\mathbf{k}))[\partial M(\mathbf{k},\epsilon(\mathbf{k}))/\partial\epsilon],$$

giving the solution for ϵ

$$\epsilon=\epsilon_0+\epsilon(\mathbf{k})+[M(\mathbf{k},\epsilon(\mathbf{k}))-\epsilon_0]/[1-\partial M(\mathbf{k},\epsilon(\mathbf{k}))/\partial\epsilon], \tag{97}$$

where from Eq. (42)

$$\epsilon_0=M(\mathbf{k}_0,\epsilon(\mathbf{k}_0))=\mu-\epsilon(\mathbf{k}_0).$$

We note that Eq. (97), owing to the ϵ_0 in the denominator of our G_0, is different from the corresponding equation used by DuBois[51]

$$\epsilon=\epsilon(\mathbf{k})+M(\mathbf{k},\epsilon(k))(1+\partial M/\partial\epsilon).$$

In particular the cancellations mentioned by him between $M^{(1)}\partial M^{(1)}/\partial\epsilon$ and the noncrossed second order term of $M^{(2)}$ are taken into account in Eq. (97), cf. Sec. 6. The real and imaginary parts of the last term in Eq. (97) are given in Table IV under the headings E_1 and E_2. In Table IV we have also given the screened exchange approximation MS and Pines' approximation MP. We see that the difference between E_1 and MS is substantial; they even have opposite signs for $r_s>1$. Both E_1 and MS have a weak $\mathbf{k}$ dependence compared to MP. This is also illustrated in Fig. 9.[45] The almost horizontal curves give $E_1+\epsilon_0$ and the dashed curves give Pines' approximation. For comparison the kinetic energy $\epsilon(\mathbf{k})$ and the Hartree-Fock approximation for M are also drawn. The infinite slope of the HF curve at $\mathbf{k}=\mathbf{k}_0$ is barely noticeable, owing to the weakness of a logarithmic singularity.

We note that *the* HF *energies deviate from the true*

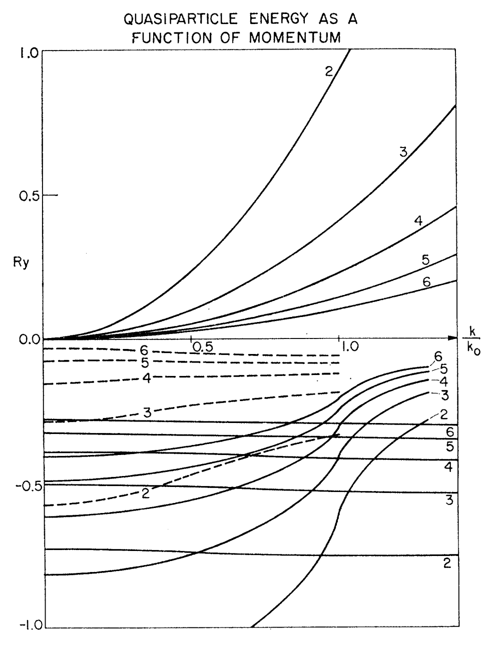

FIG. 9. Quasiparticle energy as a function of momentum. Above the axis: Free-particle part$=(\hbar^2k^2/2m)$. Below the axis: Exchange and correlation part. Dashed curve: Pines' approximation (Ref. 45). Curves with infinite slope at $\mathbf{k}=\mathbf{k}_0$: HF. Almost flat curves: E_1 in Table IV. The r_s value is indicated for each curve.

[45] D. Pines, Ref. 31, p. 407. The value of β in his Eq. (8.1) is taken as $\beta=0.375r_s^{1/2}$. This is the value used by V. Heine, Proc. Roy. Soc. (London) **A240**, 340 (1957) in his calculation on Al.

TABLE IV. Quasiparticle energy in the momentum representation.

The full quasiparticle energy $=\epsilon(\mathbf{k})+M(\mathbf{k}_0,\epsilon(\mathbf{k}_0))+$tabulated quantity, where $\epsilon(\mathbf{k})$ is the kinetic energy, $(\hbar^2\mathbf{k}^2/2m)$. The energies in the table are expressed in rydbergs. The Fermi momentum is $|\mathbf{k}_0|$.

$M=M(\mathbf{k},\epsilon(\mathbf{k}))-M(\mathbf{k}_0,\epsilon(\mathbf{k}_0))$; M in the RPA
$Z^{-1}=1-\partial M(\mathbf{k},\epsilon(\mathbf{k}))/\partial\epsilon$; M in the RPA
$E=MZ$
$\mathrm{MS}=M(\mathbf{k})-M(\mathbf{k}_0)$; M from a screened exchange potential
$\mathrm{MP}=M(\mathbf{k})-M(\mathbf{k}_0)$; M from Pines' approximation[a] with

$\beta=0.375r_s^{1/2}$. This is essentially the same β value as used by V. Heine[b] in his paper on the band structure of Al.

r_s		$k/k_0=0$	0.2	0.4	0.6	0.8	1.0	1.2	1.4
1	M_1	−0.1286	−0.1232	−0.1014	−0.0735	−0.0428	0	+0.0407	0.0459
	M_2	0.2323	0.2130	0.1608	0.0910	0.0284	0	−0.0279	−0.0948
	Re Z^{-1}	1.270	1.241	1.216	1.193	1.168	1.164	1.142	1.151
	Im Z^{-1}	0.186	0.150	0.108	0.064	0.021	0	0.017	0.040
	E_1	−0.0729	−0.0774	−0.0711	−0.0574	−0.0362	0	0.0353	0.0370
	E_2	0.1936	0.1809	0.1386	0.0794	0.0250	0	−0.0250	−0.0837
	MS	−0.2401	−0.2283	−0.1940	−0.1403	−0.0731	0	0.0709	0.1339
	MP	−0.7208	−0.6879	−0.5860	−0.4023	−0.1824	0		
2	M_1	0.0123	0.0112	0.0086	0.0039	−0.0004	0	0.0009	−0.0075
	M_2	0.0976	0.0882	0.0642	0.0349	0.0105	0	−0.0105	−0.0367
	Re Z^{-1}	1.426	1.413	1.387	1.354	1.318	1.302	1.275	1.284
	Im Z^{-1}	0.273	0.224	0.161	0.095	0.032	0	0.026	0.061
	E_1	0.0210	0.0174	0.0114	0.0047	−0.0001	0	0.0005	−0.0072
	E_2	0.0644	0.0597	0.0450	0.0255	0.0080	0	−0.0082	−0.0282
	MS	−0.0590	−0.0561	−0.0477	−0.0346	−0.0182	0	0.0184	0.0359
	MP	−0.2440	−0.2276	−0.1766	−0.1034	−0.0489	0		
3	M_1	0.0268	0.0253	0.0205	0.0132	0.0056	0	−0.0052	−0.0147
	M_2	0.0534	0.0482	0.0350	0.0190	0.0057	0	−0.0059	−0.0208
	Re Z^{-1}	1.521	1.537	1.525	1.492	1.455	1.429	1.400	1.407
	Im Z^{-1}	0.313	0.261	0.192	0.116	0.039	0	0.033	0.078
	E_1	0.0238	0.0212	0.0161	0.0098	0.0040	0	−0.0038	−0.0112
	E_2	0.0302	0.0278	0.0209	0.0120	0.0038	0	−0.0041	−0.0142
	MS	−0.0230	−0.0219	−0.0187	−0.0137	−0.0072	0	0.0075	0.0149
	MP	−0.0998	−0.0889	−0.0569	−0.0344	−0.0176	0		
4	M_1	0.0262	0.0250	0.0206	0.0139	0.0065	0	−0.0064	−0.0153
	M_2	0.0336	0.0304	0.0222	0.0121	0.0037	0	−0.0038	−0.0137
	Re Z^{-1}	1.576	1.629	1.639	1.614	1.580	1.547	1.518	1.525
	Im Z^{-1}	0.334	0.282	0.211	0.130	0.044	0	0.038	0.091
	E_1	0.0202	0.0180	0.0141	0.0092	0.0042	0	−0.0043	−0.0105
	E_2	0.0170	0.0155	0.0117	0.0068	0.0022	0	−0.0024	−0.0084
	MS	−0.0110	−0.0105	−0.0090	−0.0066	−0.0035	0	0.0037	0.0074
	MP	−0.0334	−0.0252	−0.0126	−0.0095	−0.0060	0		
5	M_1	0.0231	0.0223	0.0186	0.0129	0.0063	0	−0.0064	−0.0144
	M_2	0.0230	0.0209	0.0154	0.0085	0.0026	0	−0.0027	−0.0099
	Re Z^{-1}	1.602	1.699	1.738	1.725	1.697	1.660	1.630	1.637
	Im Z^{-1}	0.347	0.296	0.225	0.141	0.049	0	0.042	0.102
	E_1	0.0167	0.0148	0.0117	0.0078	0.0038	0	−0.0040	−0.0091
	E_2	0.0170	0.0097	0.0074	0.0043	0.0014	0	−0.0016	−0.0055
	MS	−0.0059	−0.0057	−0.0049	−0.0036	−0.0019	0	0.0020	0.0040
	MP	+0.0035	0.0090	0.0057	0.0012	−0.0008	0		
6	M_1	0.0201	0.0195	0.0164	0.0116	0.0058	0	−0.0060	−0.0132
	M_2	0.0168	0.0152	0.0113	0.0063	0.0019	0	−0.0021	−0.0075
	Re Z^{-1}	1.609	1.753	1.825	1.827	1.807	1.766	1.738	1.745
	Im Z^{-1}	0.354	0.305	0.236	0.150	0.052	0	0.046	0.112
	E_1	0.0141	0.0123	0.0096	0.0066	0.0032	0	−0.0035	−0.0078
	E_2	0.0073	0.0065	0.0049	0.0029	0.0010	0	−0.0011	−0.0038
	MS	−0.0034	−0.0033	−0.0028	−0.0021	−0.0011	0	0.0012	0.0023
	MP	0.0264	0.0234	0.0135	0.0061	0.0017	0		

[a] D. Pines, Ref. 31, p. 407.
[b] V. Heine, Proc. Roy. Soc. **A240**, 340 (1957).

quasiparticle energies in qualitatively the same way for an electron gas as for alkali atoms, though on a largely magnified scale, cf. Sec. 4.

By comparing M with E in Table IV we find that the factor Z has a large influence. For $r_s=1$ we note an anomaly. E_1 drops sharply in going from $q=0$ to $q=0.1$ before it starts rising again. This may be due to either inaccuracies in the Z values or to a discontinuity in the derivative $\partial E(\mathbf{k})/\partial k_x$. There are however no indications of such a discontinuity in $M(\mathbf{k},\epsilon(\mathbf{k}))$.

The accuracy of $E(q)$ is not good enough to permit a more detailed statement about its second derivative than the general observation that on the average it is small compared to $\epsilon''(q)=2(2/\alpha r_s)^2$ Ry. This follows from the fact that $E'(0.5)$ is small compared to $\epsilon'(0.5)=(2/\alpha r_s)^2$ Ry [see Table VI which gives $E'(0.5)/\epsilon'(0.5)$

under the heading $f_e^{(1)}$, f_0, RPA$^{(b)}$], combined with the formula,

$$\frac{1}{0.5}\int_0^{0.5} E''(q)/\epsilon''(0.5)dq = E'(0.5)/\epsilon'(0.5). \quad (98)$$

We have also calculated $M(r,\mu)$ from the formula,

$$M(r,\mu) = \left(\frac{k_0}{\pi}\right)^3 \int e^{i\mathbf{q}\cdot\mathbf{x}} M(q,\mu)d\mathbf{q} = \frac{8e^2k_0^4}{\pi^3}\frac{1}{x}\int_0^\infty dq$$
$$\times \int_0^\infty du\left(\frac{1}{\epsilon(q,iu)}-1\right)\frac{\sin qx}{qx}e^{-(a-0.125)^{1/2}x}$$
$$\times \cos(a+0.125)^{1/2}x; \quad a=\tfrac{1}{2}(u^2+0.0625)^{1/2}; \quad x=2k_0r. \quad (99)$$

The result is given in Fig. 10. Judging from the values of $M(q,\mu)$ at $q=0.4$, 0.5, and 0.6 it varies considerably faster with q than $M(q,\epsilon(q))$ and $E(q)$. $M'(0.5,\mu)/\epsilon'(0.5)$ equals 0.18, 0.39, and 0.62 for $r_s=1$, 3, and 6, respectively. The variation is however still mild compared to the logarithmic singularity of $M^{\mathrm{HF}}(q)$, which can be seen by the suppression of long range oscillations in $M(r,\mu)$. Since $rM(r,\mu)$ extends out to about $r=a_0r_s$, then $|\mathbf{k}|M(\mathbf{k},\mu)$ is essentially different from zero only for k smaller than $2\pi/r=(2\pi/a_0r_s)\cong 3k_0$. Since $E(\mathbf{k})$ varies more slowly with $\mathbf{k}$ than does $M(\mathbf{k},\mu)$ it is probable that $|\mathbf{k}|E(\mathbf{k})$ extends further out than $3k_0$. In that case the nonlocal potential corresponding to $E(\mathbf{k})$ will have a still smaller range than $M(r,\mu)$ *which speaks in favor of using electron-gas results in a local density approximation for a metal.*

We conclude this section with a comment on the Coulomb hole plus screened exchange approximation. Returning to Eq. (13) we see that the integral has a factor $\exp[i(\epsilon-\epsilon_s)(\tau/\hbar)][\theta(\tau)-\theta(\mu-\epsilon_s)]$. The Coulomb hole comes from $\theta(\tau)$ and the screened exchange from $\theta(\mu-\epsilon_s)$ when we put the exponential equal to 1. If we evaluate the contribution to M involving $\theta(\mu-\epsilon_s)$ without approximation, we obtain an energy-dependent screened exchange,

$$M^{\mathrm{ex}}(q,u) = -\frac{4}{\pi\alpha r_s}\int_{-1}^{1} d\xi \times \int dq'\frac{\theta(0.25-q^2-q'^2-2qq'\xi)}{\epsilon(q',\,u-q^2-q'^2-2qq'\xi)}\,\mathrm{Ry}, \quad (100)$$

which can be compared with the energy-independent screened exchange of Eq. (89). It has been suggested[4] that the energy dependence should have only a small influence and to check that the integral in Eq. (100) was evaluated for $u=q^2$. Compared to the energy-independent screened exchange the magnitude of $M^{\mathrm{ex}}(0.5,0.25)$ agreed quite well, being 3% and 8% smaller for $r_s=1$ and 6, respectively. The slope at $q=0.5$ on the other hand was larger by 4%, 29% and 91% for $r_s=1$, 3, and 6, respectively. The total variation between $q=0$ and $q=0.5$ was larger by 3% and smaller by 27% and 88% for $r_s=1$, 3, and 6, respectively. The two expressions thus agree poorly except for high densities.

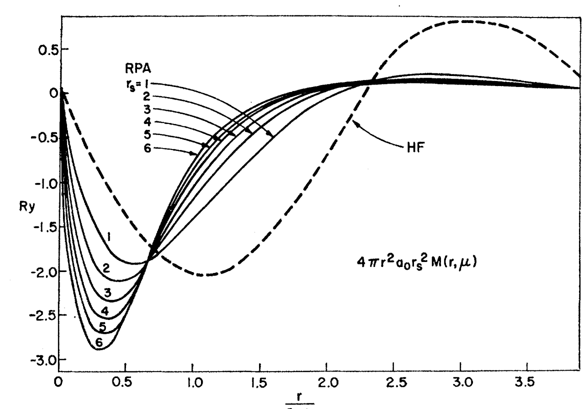

FIG. 10. Self-energy operator as a nonlocal potential. We have multiplied $M(r,\mu)$ by a factor $4\pi r^2 a_0 r_s$ from the volume element $4\pi r^2 dr = 4\pi r^2 a_0 r_s dx$, and by an extra r_s to make the HF curve r_s independent.

10. ELECTRON GAS: THE QUASIPARTICLE INTERACTION

The expansion of the quasiparticle interaction f of the Landau theory of a Fermi liquid is given in Eqs. (31) and (34) up to second order in the screened interaction W. It is convenient to use dimensionless quantities and we redefine f by

$$\delta E_\sigma(\mathbf{k}) = \frac{4\pi e^2}{k_0^2}\frac{1}{(2\pi)^3}\frac{\pi}{\alpha r_s}\sum_{\sigma'}\int f_{\sigma\sigma'}(\mathbf{k},\mathbf{k}')\delta n_{\sigma'}(\mathbf{k}')d\mathbf{k}', \quad (101)$$

where $E_\sigma(\mathbf{k})$ and $\delta n_\sigma(\mathbf{k})$ are defined as in Eq. (30). Writing f as

$$f_{\sigma\sigma'} = f_0 + f_e\delta_{\sigma\sigma'}; \quad f_e = f_e^{(1)} + f_e^{(2)}, \quad (102)$$

we have the following simple expressions[46] for the specific heat C and the paramagnetic susceptibility χ,

$$C_0/C = 1 - \int_0^\pi [2f_0(\theta)+f_e(\theta)]\cos\theta\sin\theta d\theta,$$
$$\chi_0/\chi = C_0/C + \int_0^\pi f_e(\theta)\sin\theta d\theta, \quad (103)$$

where C_0 and χ_0 are the values for a noninteracting or Sommerfeld electron gas and θ is the angle between $\mathbf{k}$ and $\mathbf{k}'$. Both $\mathbf{k}$ and $\mathbf{k}'$ have the magnitude $|\mathbf{k}_0|$.

[46] See e.g., P. Nozières in Ref. 2.

With our present definition of f, Eq. (101), using Green's functions according to Eq. (41) and dimensionless integration variables according to Eq. (56) we have

$$f_e^{(1)} = -V(\kappa,0)\,,$$

$$f_e^{(2)} = -\frac{i}{\pi^2}\int \frac{V(q_1,u_1)d\mathbf{q}_1du_1}{u_1-q_1^2-2\mathbf{q}\cdot\mathbf{q}_1}\left[\frac{2V(\kappa,0)}{u_1-q_1^2-2\mathbf{q}'\cdot\mathbf{q}_1} - \frac{V(\mathbf{q}_1+\boldsymbol{\kappa},\, u_1)}{u_1+q_1^2-2\mathbf{q}'\cdot\mathbf{q}_1}+\frac{V(\mathbf{q}_1+\boldsymbol{\kappa},\, u_1)}{u_1-q_1^2-2\mathbf{q}\cdot\mathbf{q}_1}\right], \tag{104}$$

$$f_0 = \frac{i}{\pi^2}\int \frac{V^2(q_1,u_1)d\mathbf{q}_1du_1}{u_1-q_1^2-2\mathbf{q}\cdot\mathbf{q}_1}\times\left[\frac{1}{u_1-q_1^2-2\mathbf{q}'\cdot\mathbf{q}_1}-\frac{1}{u_1+q_1^2-2\mathbf{q}'\cdot\mathbf{q}_1}\right],$$

where we have omitted the z^2 factors and used the notation

$$V(q,u) = (\lambda/4q^2\epsilon(q,u));\quad \lambda=\alpha r_s/\pi = r_s/6.03;$$
$$\boldsymbol{\kappa} = \mathbf{q}-\mathbf{q}' = (\mathbf{k}-\mathbf{k}')/(2k_0); \tag{105}$$
$$\kappa^2 = \tfrac{1}{2}(1-\cos\theta) = \sin^2(\theta/2)\,.$$

As discussed in Sec. 5, we can obtain rough approximations by replacing $W(\mathbf{k},\epsilon)$ by $W(\mathbf{k},0)$ or, in the present notation, replacing $V(q,u)$ by $V(q,0)$. The expressions for $f_e^{(2)}$ and f_0 then become,

$$f_e^{(2)} = \frac{1}{\pi}\int V(q_1,0)d\mathbf{q}_1\left[\frac{2V(\kappa,0)\eta_1}{\boldsymbol{\kappa}\cdot\mathbf{q}_1}-\frac{V(\mathbf{q}_1+\boldsymbol{\kappa},\,0)\eta_2}{(\boldsymbol{\kappa}+\mathbf{q}_1)\cdot\mathbf{q}_1}\right],$$

$$f_0 = -\frac{1}{\pi}\int V^2(q_1,0)d\mathbf{q}_1\left(\frac{\eta_1}{\boldsymbol{\kappa}\cdot\mathbf{q}_1}-\frac{\eta_2}{(\boldsymbol{\kappa}+\mathbf{q}_1)\cdot\mathbf{q}_1}\right), \tag{106}$$

$$\eta_1 = \theta(0.25-(\mathbf{q}+\mathbf{q}_1)^2)-\theta(0.25-(\mathbf{q}'+\mathbf{q}_1)^2)\,,$$
$$\eta_2 = \theta(0.25-(\mathbf{q}+\mathbf{q}_1)^2)-\theta((\mathbf{q}'+\mathbf{q}_1)^2-0.25)\,.$$

Using the G defined in Eq. (41) we have from Eqs. (27) and (28)

$$C_0/C = 1+z\left[\frac{d}{dk}M(\mathbf{k},\epsilon(\mathbf{k}))\bigg/\left(\frac{d}{dk}\epsilon(\mathbf{k})\right)\right]. \tag{107}$$

Neglecting the z factors, the contributions to C_0/C in Eq. (107) are identical with those in Eq. (103) according to the following correspondences:

$$f_e^{(1)}\,,\ \text{Eq. (104)} \rightarrow M^c\,,\ \text{Eq. (89)}\,,$$
$$f_0\,,\ \text{Eq. (104)} \rightarrow M^r\,,\ \text{Eq. (91)}\,, \tag{108}$$
$$f_e^{(2)}\,,\ \text{Eq. (106)} \rightarrow M^{(2)}\,,\ \text{Eq. (78)}\,.$$

The first and third correspondences are easily checked by straightforward differentiation of M^c and $M^{(2)}$. To prove the second correspondence we write the expressions for M^r in the form

$$M^r(\mathbf{k},\epsilon(\mathbf{k})) = \frac{2}{(2\pi)^4}\int d\mathbf{k}''\int_0^\infty dw\frac{\epsilon(\mathbf{k}+\mathbf{k}'')-\epsilon(\mathbf{k})}{(\epsilon(\mathbf{k}+\mathbf{k}'')-\epsilon(\mathbf{k}))^2+w^2}\times(W(\mathbf{k}'',iw)-W(\mathbf{k}'',0)). \tag{109}$$

We then perform a partial integration with respect to w, $(dW/dw=W^2dP/dw)$,

$$M^r(\mathbf{k},\epsilon(\mathbf{k})) = \frac{16}{(2\pi)^7}\int d\mathbf{k}''\int_0^\infty dw\times\arctan\frac{\epsilon(\mathbf{k}+\mathbf{k}'')-\epsilon(\mathbf{k})}{w}W^2(\mathbf{k}'',iw)\times\int d\mathbf{k}'\frac{(\epsilon(\mathbf{k}'+\mathbf{k}'')-\epsilon(\mathbf{k}'))w\theta(k_0-|\mathbf{k}'|)}{\{[\epsilon(\mathbf{k}'+\mathbf{k}'')-\epsilon(\mathbf{k}')]^2+w^2\}^2}. \tag{110}$$

The last integral in Eq. (110) can be written[47]

$$-\frac{m}{2\hbar^2k_0}\frac{w}{\mathbf{k}\cdot\mathbf{k}''}\int\frac{\mathbf{k}\cdot\mathbf{k}'\delta(|\mathbf{k}'|-k_0)d\mathbf{k}'}{[\epsilon(\mathbf{k}'+\mathbf{k}'')-\epsilon(\mathbf{k}')]^2+w^2}. \tag{111}$$

When we form $d/dk=(\mathbf{k}/k_0)\cdot d/d\mathbf{k}$ of $M^r(\mathbf{k},\epsilon(\mathbf{k}))$, the factor $(\mathbf{k}\cdot\mathbf{k}'')^{-1}$ drops out and it is relatively easy to check that we arrive at the same expression for C_0/C as when f_0 of Eq. (104) is used in Eq. (103). It is easily realized that we have the correspondence f_0, Eq. (106) $\rightarrow M^r$, Eq. (110) with $W(\mathbf{k},0)$ instead of $W(\mathbf{k},iw)$.

Thus the RPA *result for the specific heat is reproduced by $f_e^{(1)}$ and f_0 apart from a factor z.* It seems probable, although we have not been able to prove it, that if we use Eq. (43) instead of Eq. (41) for G, the *iGW* expression for M will give exactly the same result for C_0/C as $f_e^{(1)}$ and f_0 [cf. the discussion in connection with Eqs. (35) to (37)].

The numerical results for $f_e^{(1)}$, Eq. (104) and $f_e^{(2)}$, f_0, Eq. (106) are given in Table V and Fig. 11. The f's are multiplied by $\sin\theta$ to make it easier to estimate their contributions in Eq. (103). The z^2-factor is not included in Table V and Fig. 11. Since we have numerical results for $M^r[\mathbf{k},\epsilon(\mathbf{k})]$ we can evaluate the contribution to $C_0/C-1$ from f_0, Eq. (104) and compare with the contribution from the static approximation for f_0, Eq. (106). These contributions are given in Table VI under the headings (f_0,RPA) and (f_0,static). We expect similar differences between the contributions from $f_e^{(2)}$ according to Eqs. (104) and (106). The static approximation for the second-order terms in f is thus fairly rough and seems to somewhat underestimate them.

[47] We use the identity

$$\int \nabla f(\mathbf{k})\theta(|\mathbf{k}_0|-|\mathbf{k}|)d\mathbf{k} = \int(\mathbf{k}/|\mathbf{k}|)f(\mathbf{k})\delta(|\mathbf{k}_0|-|\mathbf{k}|)d\mathbf{k}.$$

TABLE V. Quasiparticle interactions multiplied by $\sin\theta$.

		$r_s=1$			$r_s=2$			$r_s=3$	
θ	$f_e^{(1)}$	f_0	$f_e^{(2)}$	$f_e^{(1)}$	f_0	$f_e^{(2)}$	$f_e^{(1)}$	f_0	$f_e^{(2)}$
$\frac{\pi}{8}\times 0$	0	0	0	0	0	0	0	0	0
1	−0.0788	−0.0009	−0.0187	−0.0869	−0.0032	−0.0264	−0.0900	−0.0069	−0.0285
2	−0.0969	−0.0018	−0.0188	−0.1274	−0.0067	−0.0322	−0.1424	−0.0141	−0.0367
3	−0.0842	−0.0030	−0.0112	−0.1271	−0.0106	−0.0217	−0.1531	−0.0220	−0.0250
4	−0.0656	−0.0043	−0.0038	−0.1081	−0.0152	−0.0066	−0.1379	−0.0304	−0.0044
5	−0.0473	−0.0062	0.0019	−0.0824	−0.0201	0.0070	−0.1095	−0.0383	0.0156
6	−0.0307	−0.0084	0.0055	−0.0553	−0.0241	0.0159	−0.0755	−0.0429	0.0286
7	−0.0151	−0.0095	0.0063	−0.0278	−0.0231	0.0171	−0.0386	−0.0374	0.0289
$7+\frac{1}{3}$		−0.0091	0.0057		−0.0202	0.0148		−0.0318	0.0246
$7+\frac{2}{3}$		−0.0066	0.0041		−0.0139	0.0105		−0.0211	0.0171
$7+\frac{5}{6}$		−0.0042	0.0025		−0.0085	0.0065		−0.0127	0.0104
8	0	0	0	0	0	0	0	0	0

		$r_s=4$			$r_s=5$			$r_s=6$	
θ	$f_e^{(1)}$	f_0	$f_e^{(2)}$	$f_e^{(1)}$	f_0	$f_e^{(2)}$	$f_e^{(1)}$	f_0	$f_e^{(2)}$
$\frac{\pi}{8}\times 0$	0	0	0	0	0	0	0	0	0
1	−0.0917	−0.0116	−0.0273	−0.0927	−0.0173	−0.0241	−0.0933	−0.0238	−0.0192
2	−0.1512	−0.0237	−0.0354	−0.1571	−0.0350	−0.0299	−0.1613	−0.0480	−0.0214
3	−0.1706	−0.0363	−0.0220	−0.1832	−0.0530	−0.0141	−0.1926	−0.0718	−0.0024
4	−0.1510	−0.0488	0.0027	−0.1770	−0.0699	0.0141	−0.1905	−0.0932	0.0290
5	−0.1311	−0.0594	0.0276	−0.1486	−0.0827	0.0425	−0.1632	−0.1078	0.0510
6	−0.0924	−0.0634	0.0432	−0.1067	−0.0852	0.0593	−0.1190	−0.1080	0.0767
7	−0.0480	−0.0522	0.0412	−0.0561	−0.0673	0.0538	−0.0633	−0.0826	0.0667
$7+\frac{1}{3}$		−0.0430	0.0347		−0.0544	0.0445		−0.0647	0.0549
$7+\frac{2}{3}$		−0.0281	0.0236		−0.0349	0.0299		−0.0417	0.0360
$7+\frac{5}{6}$		−0.0167	0.0143		−0.0206	0.0179		−0.0244	0.0215
8	0	0	0	0	0	0	0	0	0

From Table V and Fig. 11 we see that *the first-order term in f is appreciably larger than the second-order terms for the higher metallic densities*. The convergence of the expansion for f, however, does not seem to be as good as that for μ.

From the results for $f_e^{(2)}$ and for $M^{(2)}(0,0)$ we can estimate the magnitude of $M^{(2)}[\mathbf{k},\epsilon(\mathbf{k})]$ at $\mathbf{k}=\mathbf{k}_0$. The derivative of $M^{(2)}[\mathbf{k},\epsilon(\mathbf{k})]$ relative to that of $\epsilon(\mathbf{k})$ at $\mathbf{k}=\mathbf{k}_0$ is roughly given by the value of ($f_e^{(2)}$, static) in Table VI. Taking into account that $M^{(2)}[\mathbf{k},\epsilon(\mathbf{k})]$ should flatten out at small $\mathbf{k}$ by introducing an extra factor of 0.5, we arrive at the estimate of $M^{(2)}[\mathbf{k}_0,\epsilon(\mathbf{k}_0)]$ which was given in Sec. 8, namely 0.04–0.02 Ry for r_s varying from 3 to 6. For smaller r_s,$M^{(2)}$ becomes larger and the ratio $M^{(2)}/M^{(1)}$ smaller.

The influence of the errors in the second order terms of f is suppressed since they should cancel each other to a large extent. This can be seen in Table VI by comparing the columns (f_0, $f_e^{(2)}$, static) with ($f_e^{(1)}$, RPA) or (f_e, f_0, static).

In Fig. 12[48–50] the results for the specific heat are plotted. The series expansion in r_s, given by DuBois,[51] starts to deviate from our result already at $r_s=0.5$ and for $r_s>1$ it is obviously wrong. Pines' result, which is given by $f_e^{(1)}$ with $W(r,\epsilon)=(e^2/r)S(r)$ and $S(r)$ according to Eq. (63), is qualitatively similar to ours but exaggerates the difference between C and C_0. Silverstein[52] has recently tried to include the second-order term in M by an interpolation procedure similar to that used by Nozières and Pines[53] for the correlation energy. Silverstein expressed $C_0/C-1$ as an integral over the momentum transfer q, using RPA for small q and unscreened perturbation theory up to second order for large q. His results are however more negative than the RPA results (compare the last two columns in Table VI) even though the second-order terms give a positive contribution to $C_0/C-1$. This probably is due to his use of a series expansion in q for the RPA part of his integrand rather than the complete RPA expression. Silverstein's result[54] for χ_0/χ minus his result for C_0/C are given in the last column of Table VII. They agree roughly with our results from $f_e^{(1)}$ without the z^2 factor.

Since $f_e^{(1)}$ gives the largest contribution to the specific heat as well as to the paramagnetic susceptibility, it is of interest to examine how sensitive the results are to the precise form of $f_e^{(1)}$. The series expansion of the RPA expression for $\epsilon(\kappa,0)$ is easily

[48] D. Pines, Ref. 31, p. 408, Eq. (8.4). ($\beta=0.353r_s^{1/2}$).
[49] D. F. DuBois, Ann. Phys. **8**, 24 (1959).
[50] S. D. Silverstein, Phys. Rev. **128**, 631 (1962).
[51] D. F. DuBois, Ann. Phys. (N. Y.) **8**, 24 (1959).

[52] S. D. Silverstein, Phys. Rev. **128**, 631 (1962).
[53] P. Nozières and D. Pines, Phys. Rev. **111**, 442 (1958).
[54] S. D. Silverstein, Phys. Rev. **130**, 1703 (1963).

TABLE VI. Different contributions to $(C_0/C)-1$.

r_s	$f_e^{(1)}$ RPA	f_0 RPA	f_0 static	$f_e^{(2)}$ static	f_0, $f_e^{(2)}$ static	f_e, f_0 static	$f_e^{(1)}$ TF	f_e, f_0 static[a]	$f_e^{(1)}$, f_0 RPA[b]	Silverstein
1	0.0489	−0.0157	−0.0127	0.0184	0.0058	0.0547	0.0495	0.0404	0.0285	0.029
2	0.0498	−0.0419	−0.0304	0.0351	0.0047	0.0545	0.0518	0.0322	0.0061	−0.039
3	0.0451	−0.0712	−0.0482	0.0477	−0.0005	0.0446	0.0493	0.0218	−0.0183	−0.080
4	0.0392	−0.1017	−0.0649	0.0576	−0.0073	0.0319	0.0460	0.0133	−0.0404	−0.125
5	0.0332	−0.1326	−0.0808	0.0657	−0.0151	0.0181	0.0429	0.0066	−0.0599	−0.179
6	0.0275	−0.1635	−0.0954	0.0726	−0.0228	0.0047	0.0396	0.0015	−0.0770	−0.232

[a] Including the renormalization factor z^2.
[b] Including the renormalization factor z.

obtained from Eq. (57), and is

$$\epsilon(\kappa,0)=1+(\lambda/\kappa^2)(1-(\kappa^2/3)-(\kappa^4/15) -(\kappa^6/35)-\cdots);\quad |\kappa|<1 \qquad (112)$$
$$\epsilon(1,0)=1+\tfrac{1}{2}\lambda.$$

The first two terms in $\epsilon(\kappa,0)$ give the TF approximation,

$$f_e^{(1)}=-(\lambda/4(\kappa^2+\lambda));\quad \kappa^2=\sin^2(\theta/2), \qquad (113)$$

while the first three terms give the same expressions as Eq. (113) but with λ replaced by $\lambda/(1-\frac{1}{3}\lambda)$. Using Eq. (113) for f gives

$$\begin{aligned} C_0/C&=1-\lambda-\lambda(\lambda+\tfrac{1}{2})\ln(\lambda/(1+\lambda)),\\ \chi_0/\chi&=1-\lambda-\lambda^2\ln(\lambda/(1+\lambda)). \end{aligned} \qquad (114)$$

By comparing ($f_e^{(1)}$,TF) and ($f_e^{(1)}$,RPA) in Table VI and ($f_e^{(1)}$,TF) and $f_e^{(1)}$ in Table VII, we see that *the* TF *expression Eq. (114) gives a quite reasonable result.*

Eq. (114) can also be compared with the high-density results[55,56]

$$\begin{aligned} C_0/C&=1-\lambda-\lambda/2\ln\lambda,\\ \chi_0/\chi&=1-\lambda-\lambda^2/2(\ln\lambda-1.534). \end{aligned} \qquad (115)$$

Thus in the high-density limit the lowest order term in f correctly reproduces the $\lambda\ln\lambda$ and λ terms. It may be noted that while the HF expression for C_0/C diverges, the HF expression for χ_0/χ, namely, $1-\lambda$, gives a reasonable high-density description. Numerically the expressions for χ_0/χ according to Eqs. (114) and (115) are not too different at high densities. At $r_s=1$ they are, respectively, 0.888 and 0.879.

Osaka[57] has recently calculated C_0/C in what is stated to be the RPA. His result is identical[15] with that of Eq. (114) when λ is replaced by $\lambda/(1-\lambda/3)$. He used a relation between specific heat and polarization propagator which was derived from Eq. (A1) in his paper. Equation (A1) is however not quite correct since the μ factors should not be there.

TABLE VII. Different contributions to $\chi_0/\chi-C_0/C$.

r_s	$f_e^{(1)}$	$f_e^{(2)}$	f_e	f_e[a]	$f_e^{(1)}$, TF	Silverstein
1	−0.1686	−0.0149	−0.1835	−0.1355	−0.1617	−0.157
2	−0.2459	−0.0177	−0.2636	−0.1566	−0.2305	−0.228
3	−0.2980	−0.0070	−0.3050	−0.1494	−0.2741	−0.301
4	−0.3367	0.0141	−0.3226	−0.1347	−0.3049	−0.350
5	−0.3670	0.0431	−0.3240	−0.1176	−0.3280	−0.384
6	−0.3915	0.0784	−0.3131	−0.1004	−0.3460	−0.360

[a] Including the renormalization factor z^2.

Watabe[15] has recently made an analysis of the influence of Coulomb correlations on metallic properties using the Landau Fermi-liquid Theory. He approximates f by $f_e^{(1)}$, [cf. Eqs. (104) and (105)] neglecting higher order terms and the z^2 factor. For $\epsilon(\kappa,0)$, he takes the limiting expression[58] for small κ

$$\epsilon(\kappa,0)=1+(\lambda\gamma/\kappa^2), \qquad (116a)$$

$$\gamma^{-1}=\chi_0/\chi+2\int_0^\pi f_0(\theta)\sin\theta d\theta. \qquad (116b)$$

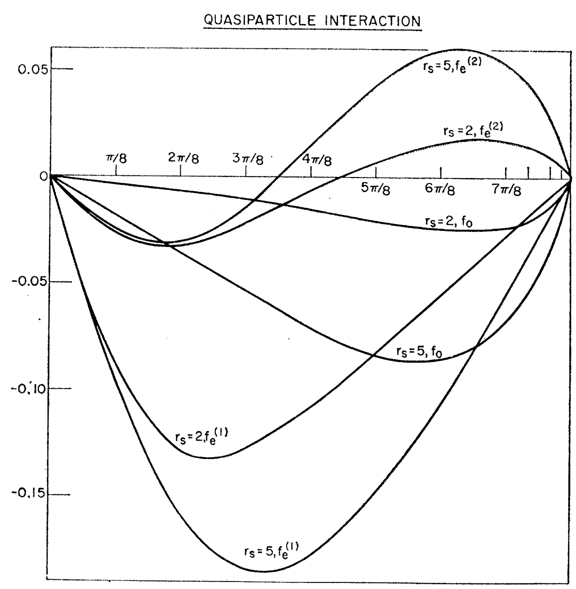

FIG. 11. Quasi-particle interaction. The quasi-particle interaction f is here defined by

$$\delta E_\sigma(\mathbf{k})=\left(\frac{4\pi e^2}{k_0^2}\frac{1}{(2\pi)^3}\frac{\pi}{\alpha r_s}\right)\sum_{\sigma'}\int f_{\sigma\sigma'}(\mathbf{k},\mathbf{k}')\delta n_{\sigma'}(\mathbf{k}')d\mathbf{k}',$$

$f_{\sigma\sigma'}=f_0+(f_e^{(1)}+f_e^{(2)})\delta_{\sigma\sigma'}$. f depends only on the angle θ between $\mathbf{k}$ and $\mathbf{k}'$. In this figure, f times $\sin\theta$ is plotted against θ. $f_e^{(1)}$ is a first-order term in W, and f_0 and $f_e^{(2)}$ are of second order in W. The z^2 factor is not included in f.

[55] M. Gell-Mann, Phys. Rev. **106**, 369 (1957).
[56] K. Sawada, Phys. Rev. **112**, 328 (1958).
[57] Y. Osaka, J. Phys. Soc. Japan **17**, 547 (1962).
[58] V. P. Silin, Zh. Eksperim. i Teor. Fiz. **33**, 495 (1957) [English transl.: Soviet Phys.—JETP **6**, 387 (1958)]; S. Misawa, Progr. Theoret. Phys. (Kyoto) **27**, 840 (1962).

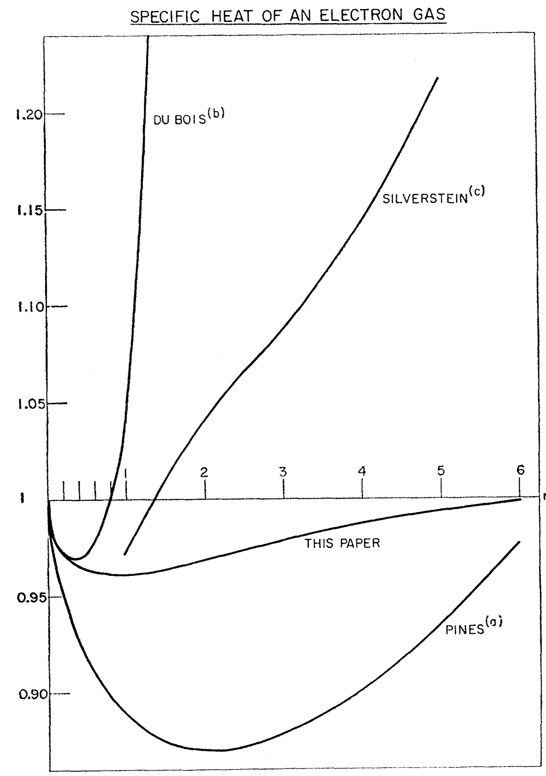

FIG. 12. Specific heat of an electron gas. The specific heat of an interacting electron gas divided by that of a non-interacting or Sommerfeld electron gas ([1+(third column from the right in Table VI)]$^{-1}$) is plotted against r_s.

Since $f_e^{(1)}$ depends on $\epsilon(\kappa,0)$ and $\epsilon(\kappa,0)$ depends on f, Watabe can write down an equation for γ from a self-consistency requirement:

$$\gamma^{-1}=1-\lambda-\lambda^2\gamma\ln(\lambda\gamma/(1+\lambda\gamma)). \tag{117}$$

Watabe's expressions for $C_0/C-1$ and $\chi_0/\chi-1$ are the same as those in Eq. (114) multiplied by γ^{-1} and with λ replaced by $\lambda\gamma$. This is obvious from Eq. (116a). Specifically he thus obtains $\chi/\chi_0=\gamma$. Watabe's result for γ ranges from 1.12 to 1.32 when r_s goes from 1 to 5. Our values for γ as given by Eq. (116b) using f_0, $f_e^{(1)}$ and $f_e^{(2)}$ with the z^2 factor agree with Watabe's within 1%. Also Glick's result[25] for γ at $r_s=2$ agrees accurately with Watabe's and ours. This is a quite remarkable coincidence, which we cannot explain.

We now make a few remarks on the analytical behavior of the different contributions to $f_{\sigma\sigma'}(\theta)$. $f_e^{(1)}(\theta)$ varies between -0.25 and $-0.25(\lambda/(1+\lambda/2))$. The slope of $f_e^{(1)}(\theta)$ is zero at θ and $\theta=\pi$. $f_0(\theta)$ and $f_e^{(2)}(\theta)$ start out with finite values at $\theta=0$ and go to infinity at $\theta=\pi$ as $\ln(1+\cos\theta)$. The coefficients of the ln term have opposite signs and roughly the same magnitude. We thus have a singular attraction between quasiparticles of opposite momenta and opposite spin giving a tendency towards a superconducting state. This effect does *not* come from the logarithmic singularity in $\epsilon(\kappa,0)$. The same effect has been noted earlier in case of a dilute Fermi gas,[59] and is there supposed to disappear when higher order terms are taken into account. To see if this attraction might be strong enough to make a spherical Fermi surface unstable, we considered the following distortion,

$$1+\delta>k/k_0>1,\quad \theta<\eta:\qquad \delta n_+(k,\theta)=1$$
$$1+\delta>k/k_0>1,\quad \theta>\pi-\eta:\quad \delta n_-(k,\theta)=1$$
$$1>k/k_0>1-\tfrac{1}{4}\eta^2\delta:$$
$$\delta n_+(k,\theta)=\delta n_-(k,\theta)=-1\,,\quad \delta\to 0\,,\quad \eta\to 0\,.$$

The lowering in energy from f relative to the increase in energy from E then becomes $a\eta^2\ln\eta$ where a, the coefficient of the singular term in f, ranges between 0.015 and 0.038 when r_s goes from 1 to 6. The attraction is thus far too weak to be of any importance.

It should be pointed out that it is not clear if there should be a z^2 factor in f when we use an approximation G_0 instead of the self-consistent G. To see this we use the results from Appendix B and write

$$E=\sum_k^{occ}[\epsilon(\mathbf{k})+V_{\text{eff}}(\mathbf{k})]+\Delta E\,,$$

$$\Delta E=\frac{i}{(2\pi)^4}\Omega\int[\phi(k';G)+e^{i\epsilon\Delta} \tag{118}$$
$$\times\mathrm{Tr}(V_{\text{eff}}G+G_0^{-1}G-1-\ln G_0^{-1}G)]dk'_{(s)}\,,$$

$$G_0(\mathbf{k},\epsilon)=(\epsilon-\epsilon(\mathbf{k})-V_{\text{eff}}(\mathbf{k}))^{-1};\quad \epsilon(\mathbf{k})=(\hbar^2k^2/2m)\,.$$

Suppose now that we approximate G by G_0 in ΔE, which since ΔE is stationary might not be too serious. We then have

$$E=\sum\epsilon(\mathbf{k})+\frac{i}{(2\pi)^4}\Omega\int\phi(k';G)dk'_{(s)}\,. \tag{119}$$

Since

$$\delta G_0(k)/\delta n_{\mathbf{k}'}=2\pi i\delta(\mathbf{k}-\mathbf{k}')\delta(\epsilon-\epsilon(\mathbf{k})-V_{\text{eff}}(\mathbf{k})) \tag{120}$$

we have that

$$E(\mathbf{k})=\delta E/\delta n_{\mathbf{k}}=\epsilon(\mathbf{k})+M(\mathbf{k},\epsilon(\mathbf{k})+V_{\text{eff}}(\mathbf{k}))\,,$$
$$f(\mathbf{k},\mathbf{k}')=\delta E(\mathbf{k})/\delta n_{\mathbf{k}'}=2\pi i\,{}^0I(k,k');\qquad \epsilon=\epsilon'=\epsilon(\mathbf{k}_F)+V_{\text{eff}}(\mathbf{k}_F)\,. \tag{121}$$

Suppose on the other hand that we start from

$$E(\mathbf{k})=\epsilon(\mathbf{k})+M(\mathbf{k},E(\mathbf{k}))\,, \tag{122}$$

where M is a functional of G_0. We then have for f

$$f(\mathbf{k},\mathbf{k}')=2\pi iz\,{}^0I(k,k');\quad \epsilon=\epsilon'=\epsilon(\mathbf{k}_F)+V_{\text{eff}}(\mathbf{k}_F)\,. \tag{123}$$

The equations for f, (121) and (123), may be compared to Eq. (32). We thus get different results depending on

[59] See A. A. Abrikosov *et al.*, (Ref. 2), p. 36.

which of several exact formulas we put the approximation G_0 in. It seems hard to resolve this ambiguity without a numerical comparison with a calculation involving some energy-dependent M in the denominator of G.

11. SUMMARY

The main results from the formal analysis are (1) A set of self-consistent equations for the one-electron Green's function involving a screened potential W (Sec. 3 and Appendix A). (2) A variational formulation for each self-consistent equation (Appendix B). (3) A specific approximation for the first-order equation. This approximation has been named COHSEX and it involves a "Coulomb hole" and a screened exchange term (Sec. 4). (4) An expansion of the quasiparticle interaction $f(\mathbf{k},\mathbf{k}')$ of the Landau Fermi-liquid theory in terms of the screened potential W (Sec. 5). (5) An explicit verification that for the first- and second-order terms in W, the quasiparticle energy $E(\mathbf{k})$ and the quasiparticle interaction $f(\mathbf{k},\mathbf{k}')$ give the same result for the specific heat of an electron gas (Sec. 10).

The numerical results are primarily intended to illustrate the convergence properties of the self-consistent equations for the Green function. Without actually solving the self-consistency problem, we have been able to draw some important conclusions. These derive mainly from calculations for the electron gas but also partly from analysis of spectral data for atoms. Qualitative conclusions regarding the electron gas are expected to hold also for metals. The main conclusions are: (1) For an electron outside a closed-shell structure, COHSEX is expected to work well (Sec. 4). (2) The magnitude of the quasiparticle energy $E(\mathbf{k})$ for an electron gas is given quite well by the first-order equation (Sec. 8). To obtain a good representation of the $\mathbf{k}$ dependence of $E(\mathbf{k})$, we have to go to the second-order equation (Sec. 10). (3) The expansion for the quasiparticle interaction has much poorer convergence than that for $E(\mathbf{k})$. In particular it seems unreliable at the alkali-metal densities (Sec. 10). (4) The $\mathbf{k}$ dependence of $E(\mathbf{k})$ is very small at the Fermi surface (Secs. 9 and 10). (5) The quantitative results for $f(\mathbf{k},\mathbf{k}')$ and $\mathbf{k}$ dependence of $E(\mathbf{k})$ will probably be appreciably changed by carrying through a self-consistent solution. This might best be done by parametrizing the spectral function for the Green function and using the variational formulation. (6) The energy-dependence of the self-energy $M(\mathbf{k},\epsilon)$ is appreciable and cannot be neglected (Sec. 9). (7) The results largely confirm the values of the correlation energy for an electron gas obtained by Nozières and Pines[53] and by Gaskell.[40] In addition we give a discussion of the possible errors involved (Sec. 8). (8) The electron gas does not seem to become ferromagnetic for $r_s<7$. For higher r_s the difference between the ferromagnetic and paramagnetic energies is very small and no prediction could be made (Sec. 8).

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APPENDIX A. EXPANSION OF THE SELF-ENERGY M AND THE POLARIZATION PROPAGATOR P IN TERMS OF THE SCREENED INTERACTION W

The results in this Appendix up to Eq. (A25) are well known to the "Green's-function people". The present derivation, however, utilizes only the Schrödinger equation. It constitutes a "low-brow" version of those parts of the "high-brow" Green's-function theory that we need here.

We write the Schrödinger representation of the Hamiltonian for the system to be considered as

$$H=H_0+H_1,$$

$$H_0=\int\psi^\dagger(\mathbf{x})h(\mathbf{x})\psi(\mathbf{x})d\mathbf{x}+\frac{1}{2}\int\psi^\dagger(\mathbf{x})\psi^\dagger(\mathbf{x}')v(\mathbf{x},\mathbf{x}')\psi(\mathbf{x}')\psi(\mathbf{x})d\mathbf{x}d\mathbf{x}',\tag{A1}$$

$$H_1=\int\rho(\mathbf{x})w(\mathbf{x},t)d\mathbf{x},\quad \rho(\mathbf{x})=\psi^\dagger(\mathbf{x})\psi(\mathbf{x}),$$

where h and v are defined as in Eq. (2). We use the notation $(1)=x_1=(\mathbf{x}_1,t_1)=(\mathbf{r}_1,\zeta_1,t_1)$. The potential $w(\mathbf{x},t)$ is to be put equal to zero in the final formulas. Let the time-evolution operator for the state vectors in the Schrödinger representation be $V(t,t')$ when $w\neq0$, and $U(t,t')$ when $w\equiv0$. The Schrödinger equation then gives

$$V(t,t')=U(t,t')-i/\hbar\int_{t'}^{t}U(t,t'')H_1(t'')V(t'',t')dt''.\tag{A2}$$

The functional derivative of V with respect to w is

$$(\delta V(t,t')/\delta w(\mathbf{x}_2,t_2))=-(i/\hbar)\times\operatorname{sgn}(t-t')V(t,t_2)\rho(\mathbf{x}_2)V(t_2,t'),\tag{A3}$$

if t_2 is inside the time interval determined by t and t', otherwise $\delta V/\delta w$ is zero. We define the Heisenberg representation of the field operator by

$$\psi(\mathbf{x},t)=V(-T_0,t)\psi(\mathbf{x})V(t,-T_0),\tag{A4}$$

where T_0 is large and positive. Schrödinger's equation then gives

$$i\hbar(\partial\psi(\mathbf{x},t)/\partial t)=V(-T_0,t)\times[\psi(\mathbf{x}),H_0+H_1]V(t,-T_0).\tag{A5}$$

By evaluating the commutator in Eq. (A5), we obtain

$$\left[i\hbar\frac{\partial}{\partial t}-h(\mathbf{x})-w(\mathbf{x},t)\right]\psi(\mathbf{x},t)-\int v(\mathbf{x},\mathbf{x}')\psi^{\dagger}(\mathbf{x}',t)\psi(\mathbf{x}',t)d\mathbf{x}'\psi(\mathbf{x},t)=0\,. \tag{A6}$$

Using the facts that $d\theta(t)/dt=\delta(t)$ and $\psi(\mathbf{x})\psi^{\dagger}(\mathbf{x}')+\psi^{\dagger}(\mathbf{x}')\psi(\mathbf{x})=\delta(\mathbf{x},\mathbf{x}')$, we obtain from Eq. (A6)

$$\left[i\hbar\frac{\partial}{\partial t}-h(\mathbf{x})-w(\mathbf{x},t)\right]T(\psi(\mathbf{x},t)\psi^{\dagger}(\mathbf{x}',t'))-\int v(\mathbf{x},\mathbf{x}'')T(\psi^{\dagger}(\mathbf{x}'',t)\psi(\mathbf{x}'',t)\psi(\mathbf{x},t)\psi^{\dagger}(\mathbf{x}',t'))d\mathbf{x}''=i\hbar\delta(\mathbf{x},\mathbf{x}')\delta(t,t')\,, \tag{A7}$$

where T is the Dyson time-ordering operator. The product of four field operators in Eq. (A7) can be generated by a functional derivative. Using Eq. (A3) we have

$$(\delta/\delta w(3))V(T_0,-T_0)T(\psi(1)\psi^{\dagger}(2))=-\frac{i}{\hbar}V(T_0,-T_0)T(\psi^{\dagger}(3)\psi(3)\psi(1)\psi^{\dagger}(2))\,, \tag{A8}$$

assuming t_3 to be in the interval T_0, $-T_0$. We define the one-particle Green's function by

$$G(1,2)=-\frac{i}{\hbar}\frac{\langle N|U(-T_0,T_0)V(T_0,-T_0)T(\psi(1)\psi^{\dagger}(2))|N\rangle}{\langle N|U(-T_0,T_0)V(T_0,-T_0)|N\rangle}\,, \tag{A9}$$

where $|N\rangle$ is some state of the N-particle system with $w\equiv 0$. The definition Eq. (A9) coincides with Eq. (1) when $w\equiv 0$, and $|N\rangle$ is the ground state. From Eqs. (A7), (A8), and (A9) we have

$$\left(i\hbar\frac{\partial}{\partial t_1}-h(1)-V(1)\right)G(1,2)-i\hbar\int v(1^+,3)\frac{\delta}{\delta w(3)}G(1,2)d(3)=\delta(1,2)\,, \tag{A10}$$

where

$$V(1)=w(1)+\int v(1^+,3)\frac{\langle N|U(-T_0,T_0)V(T_0,-T_0)\psi^{\dagger}(3)\psi(3)|N\rangle}{\langle N|U(-T_0,T_0)V(T_0,-T_0)|N\rangle}d(3)\,, \tag{A11}$$

$$1^+=(\mathbf{x}_1,t_1+\Delta)\quad\text{and}\quad v(1,2)=v(\mathbf{x}_1,\mathbf{x}_2)\delta(t_1-t_2)\,.$$

The second term in Eq. (A11) comes from the functional derivative of the denominator in Eq. (A9). If we had defined the Green's function without that denominator, we would have had $\langle N|U(-T_0,T_0)V(T_0,-T_0)|N\rangle\times\delta(1,2)$ instead of $\delta(1,2)$ in Eq. (A10). That, however, would have spoiled a simple definition of the inverse of the Green's function, [cf. Eqs. (A14) and (A15) below]. We note that it is important to use $v(1^+,3)$ rather than $v(1,3)$ in Eq. (A10) in order to correctly reproduce the four operators in Eq. (A7). In Eq. (A11), on the other hand, we can replace $v(1^+,3)$ by $v(1,3)$. From Eqs. (A9) and (A11) we have

$$V(1)=w(1)-i\hbar\int v(1,3)G(3,3^+)d(3)\,. \tag{A12}$$

T_0 is to be taken large enough so that all times of interest in $G(1,2)$ lie in the interval $(-T_0,T_0)$. Equation (A10) can be derived from Schwinger's dynamical principle, cf., e.g. the first or the second paper in Ref. 2. *The present derivation of the basic Eq. (A10) has however the virtue of being very elementary and fairly short.*

We define the self-energy operator or mass operator M by

$$\left(i\hbar\frac{\partial}{\partial t_1}-h(1)-V(1)\right)G(1,2)-\int M(1,3)G(3,2)d(3)=\delta(1,2)\,. \tag{A13}$$

From the definition of the inverse Green's function

$$\int G(1,3)G^{-1}(3,2)d(3)=\delta(1,2)\,, \tag{A14}$$

follows the identity

$$\frac{\delta G(1,2)}{\delta w(3)}=-\int G(1,4)\frac{\delta G^{-1}(4,5)}{\delta w(3)}G(5,2)d(4)d(5)\,. \tag{A15}$$

Using Eqs. (A10), (A13), and (A15) we can write M as

$$M(1,2)=-i\hbar\int v(1^+,3)G(1,4)\frac{\delta G^{-1}(4,2)}{\delta w(3)}d(3)d(4)\,. \tag{A16}$$

We define the screened interaction W by

$$W(1,2)=\int v(1,3)\frac{\delta V(2)}{\delta w(3)}d(3)\,. \qquad \text{(A17)}$$

From Eqs. (A3) and (A11) it is easily seen that this definition gives the same result as Eq. (9), remembering that w has to be put equal to zero when the functional derivative has been taken. Using Eqs. (A12), (A15), and (A17) we can write W as

$$W(1,2)=v(1,2)+i\hbar\int v(1,3)v(2,4)G(4,5)\times\frac{\delta G^{-1}(5,6)}{\delta w(3)}G(6,4^+)d(3)d(4)d(5)d(6)\,. \qquad \text{(A18)}$$

Using the identity

$$\frac{\delta}{\delta w(1)}=\int\frac{\delta V(2)}{\delta w(1)}\frac{\delta}{\delta V(2)}d(2)\,, \qquad \text{(A19)}$$

W can be written

$$W(1,2)=v(1,2)+\int W(1,3)P(3,4)v(4,2)d(3)d(4)\,, \qquad \text{(A20)}$$

where

$$P(3,4)=i\hbar\int G(4,5)G(6,4^+)\frac{\delta G^{-1}(5,6)}{\delta V(3)}d(5)d(6)\,. \qquad \text{(A21)}$$

Introducing the vertex function Γ,

$$\begin{aligned}\Gamma(1,2;3)&=-(\delta G^{-1}(1,2)/\delta V(3))\\&=\delta(1,2)\delta(1,3)+(\delta M(1,2)/\delta V(3))\,,\end{aligned} \qquad \text{(A22)}$$

we finally obtain the following expressions for M and P:

$$M(1,2)=i\hbar\int W(1^+,3)G(1,4)\Gamma(4,2;3)d(3)d(4)\,, \qquad \text{(A23)}$$

$$P(1,2)=-i\hbar\int G(2,3)G(4,2^+)\Gamma(3,4;1)d(3)d(4)\,. \qquad \text{(A24)}$$

The functional derivatives of G and W can be written

$$\frac{\delta G(1,2)}{\delta V(3)}=\int G(1,4)G(5,2)\Gamma(4,5;3)d(4)d(5)\,, \qquad \text{(A25)}$$

$$\frac{\delta W(1,2)}{\delta V(3)}=\int W(1,4)W(5,2)\frac{\delta P(4,5)}{\delta V(3)}d(4)d(5)\,. \qquad \text{(A26)}$$

Equation (A25) follows immediately from Eqs. (A15) and (A22). To prove Eq. (A26) we write W in the form $W=v(1-Pv)^{-1}$ and use an identity similar to that of Eq. (A15). *From Eqs. (A22) to (A26) we can now generate series expansions in W.*

The contribution to Γ of zero order in W is

$$\Gamma^{(0)}(1,2;3)=\delta(1,2)\delta(1,3)\,. \qquad \text{(A27)}$$

The lowest order contributions to M and P are thus

$$\begin{aligned}M^{(1)}(1,2)&=i\hbar G(1,2)W(1^+,2)\,,\\P^{(0)}(1,2)&=-i\hbar G(1,2^+)G(2,1)\,.\end{aligned} \qquad \text{(A28)}$$

To obtain the first-order contribution to Γ from Eq. (A22) it is sufficient to take the functional derivative only of the explicit G in $M^{(1)}$,

$$\Gamma^{(1)}(1,2;3)=i\hbar G(1,3)G(3,2)W(1^+,2)\,. \qquad \text{(A29)}$$

This gives for M and P

$$\begin{aligned}M^{(2)}(1,2)&=(i\hbar)^2\int W(1^+,3)G(1,4)G(4,3)G(3,2)W(4^+,2)d(3)d(4)\,,\\P^{(1)}(1,2)&=-(i\hbar)^2\int G(2,3)G(4,2^+)W(3^+,4)G(3,1)G(1,4)d(3)d(4)\,.\end{aligned} \qquad \text{(A30)}$$

The second-order contribution to Γ arises both from $M^{(1)}$ and $M^{(2)}$. From $M^{(1)}$ we have

$$\begin{aligned}\Gamma^{(2)\prime}(1,2;3)=\;&i\hbar W(1^+,2)\int G(1,4)G(5,2)\Gamma^{(1)}(4,5;3)d(4)d(5)\\&+i\hbar G(1,2)\int W(1^+,4)W(5,2)(-i\hbar)(G(5,4)G(4,3)G(3,5)^++G(5,3)G(3,4)G(4,5^+))d(4)d(5)\,,\end{aligned} \qquad \text{(A31)}$$

and from $M^{(2)}$

$$\begin{aligned}\Gamma^{(2)\prime\prime}(1,2;3)=\;&(i\hbar)^2\int W(1^+,4)W(5^+,2)(G(1,3)G(3,5)G(5,4)G(4,2)\\&+G(1,5)G(5,3)G(3,4)G(4,2)+G(1,5)G(5,4)G(4,3)G(3,2))d(4)d(5)\,.\end{aligned} \qquad \text{(A32)}$$

The third-order contribution to Γ contains 49 terms, 6 from G and 6 from W in $M^{(1)}$, 3 from the G's and 4 from the W's in $M^{(2)}$ and 30 from the G's in $M^{(3)}$.

We can obviously continue in this way and generate as many terms as we wish. We can also generate infinite partial summations in W. Thus if we, e.g., decide to approximate M by $M^{(1)}$ in Eq. (A22) and to consider only the functional derivative of the explicit G, we obtain the following integral equation for Γ,

$$\Gamma(1,2;3)=\delta(1,2)\delta(1,3)+i\hbar\int W(1^+,2)\times G(1,4)G(5,2)\Gamma(4,5;3)d(4)d(5). \quad \text{(A33)}$$

Eq. (A33) generates for P the ladder-bubble sum given in Eq. (61). When we insert this Γ into Eq. (A23) we obtain for M only one diagram in each order. Thus we include the first but not the second and the third of the third-order diagrams of Fig. 1. *This does not seem to be a systematic improvement on M.* If at all an infinite summation should be made, a wider class of diagrams should be included. This conclusion is supported also by our results in Appendix B.

APPENDIX B. VARIATIONAL PRINCIPLES

We start by treating the case of an electron gas. The results are then generalized to the case of an arbitrary system. Klein[60] has proved that when we express the energy difference between the interacting and noninteracting ground states as a certain functional $\Delta E(G)$ of the one-particle Green's function G, this functional is stationary with respect to small changes of G relative to the true G. We write ΔE as[61]

$$\Delta E(G)=i\frac{\Omega}{(2\pi)^4}\int\{\Phi(k';G)+e^{i\epsilon'\Delta}\,\mathrm{Tr}[G_0^{-1}(k')G(k')-1-\ln G_0^{-1}(k')G(k')]\}dk'_{(s)}, \quad \text{(B1)}$$

where the functional Φ has the property

$$\int\delta\Phi(k';G)/\delta G(k)dk'_{(s)}=-M(k;G)e^{i\epsilon\Delta}. \quad \text{(B2)}$$

Here Ω is the volume of the system. The variable k includes spin, momentum and energy, while in $k_{(s)}$ spin is left out. Tr stands for spin summation. The functional $M(k;G)$ becomes the true $M(k)$ when G equals the true G. From Eqs. (B1) and (B2) we see that the demand that $\delta\Delta E(G)/\delta G(k)$ be zero for all k gives

$$-M(k;G)+G_0^{-1}(k)-G^{-1}(k)=0,$$

or

$$(\epsilon-\epsilon(k)-M(k;G))G(k)=1. \quad \text{(B3)}$$

[60] A. Klein, Phys. Rev. **121**, 950 (1961).
[61] See P. Nozières, (Ref. 1), pp. 221–229.

Since Eq. (B3) is satisfied for the true G, ΔE is stationary. Klein expressed Φ as an infinite sum of "skeleton" diagrams ordered after increasing powers of the bare interaction v. If we replace this Φ by some truncated expression Φ', we obtain truncated functionals $\Delta E'$ and M' from Eqs. (B1) and (B2). The functional $\Delta E'$ is stationary if and only if G is a self-consistent solution of Eq. (B3), M replaced by M'.

We will now develop expressions for Φ, that give an $M(k;G)$ expanded in the screened potential W. Equation (B3) then gives the self-consistent equations for G that we derived in Appendix A and discussed in Sec. 3. We start by writing down the expectation value of the potential energy, Eq. (7):

$$\langle V\rangle=-\frac{i}{2}\frac{\Omega}{(2\pi)^4}\int e^{i\epsilon\Delta}M(k)G(k)dk. \quad \text{(B4)}$$

The Fourier transforms of M and P, Eqs. (A23) and (A24), are

$$M(k)=\frac{i}{(2\pi)^4}\int e^{-i\epsilon'\Delta'}W(k')G(k-k')\Gamma(k,k')dk', \quad \text{(B5)}$$

$$P(k')=-\frac{i}{(2\pi)^4}\int e^{i\epsilon\Delta}G(k)G(k-k')\Gamma(k,k')dk, \quad \text{(B6)}$$

where the vertex function $\Gamma(1,2;3)$ has been regarded as a function of x_1-x_2 and x_3-x_1 in taking the Fourier transform. We note that the $P(k)$ of Eq. (B6) has to be integrated over spin to give the $P(k)$ of Eq. (24). Comparing Eqs. (B4), (B5), and (B6) we see that

$$\langle V\rangle=\frac{i}{2}\frac{\Omega}{(2\pi)^4}\int P(k')W(k')dk', \quad \text{(B7)}$$

where for $P(k')$ we have used a slightly modified expression,

$$P(k')=-\frac{i}{(2\pi)^4}\int e^{i\epsilon\Delta}e^{-i\epsilon'\Delta'}\times G(k)G(k-k')\Gamma(k,k')dk, \quad \Delta>\Delta'. \quad \text{(B8)}$$

We have to choose Δ' smaller than Δ since the limit $\Delta'\to 0$ is taken before $\Delta\to 0$ in Eq. (B4). This modification of $P(k)$ only influences its asymptotic behavior at large ϵ. It corresponds to redefining the explicit G's in P as $G^{\mathrm{new}}(k)=e^{i\epsilon\Delta}G(k)$ or $G^{\mathrm{new}}(1,2)=G(1,2^+)$. We can consider the G's appearing in Γ and W as so modified without changing Eq. (B7). The expression for $\langle V\rangle$ can be written

$$\langle V\rangle=\frac{i}{2}\frac{\Omega}{(2\pi)^4}\int\frac{v(k)\,\mathrm{Tr}P(k)}{1-v(k)\,\mathrm{Tr}P(k)}dk_{(s)}. \quad \text{(B9)}$$

Equation (B9) gives a modification of the usual relation[34] between $\langle V\rangle$ and the inverse dielectric function, the infinite constant being taken care of by the redefinition of the Green function.

The energy shift ΔE is obtained from $\langle V\rangle$ by the well-known expression

$$\Delta E=\int_0^1 \frac{d\lambda}{\lambda}\langle V\rangle, \qquad \text{(B10)}$$

where all v's in $\langle V\rangle$ are replaced λv. If we neglect the λ dependence of P we have, from Eqs. (B9) and (B10),

$$\Delta E=-\frac{i}{2}\frac{\Omega}{(2\pi)^4}\int \ln(1-v(k)\,\mathrm{Tr}P(k))dk_{(s)}. \qquad \text{(B11)}$$

Since the imaginary part of the dielectric function always has the same sign we have no trouble with the branches of the logarithm. The modification of P, Eq. (B8), occurs only when Pv is small compared to 1 and thus has no influence in this question. By taking the functional derivative of the Φ corresponding to Eq. (B11) we can find out what more terms are needed in Φ to make it satisfy Eq. (B2). *The expression for Φ which gives M up to $(n+1)$st order in W is*

$$\Phi^{(n)}(k;G)=-\frac{1}{2}\left\{\ln\left[1-v(k)\sum_{m=0}^{n}\mathrm{Tr}P^{(m)}(k)\right]+W(k)\sum_{m=0}^{n}\frac{m}{m+1}\mathrm{Tr}P^{(m)}(k)\right\}, \qquad \text{(B12)}$$

where W is defined from $P=\sum_0^n P^{(m)}$. To verify this we form the functional derivative of Eq. (B12),

$$\int\frac{\delta\Phi^{(n)}(k';G)}{\delta G(k)}dk'_{(s)}=\frac{1}{2}\int\sum_{m=0}^{n}\frac{1}{m+1}\times\left[W(k')\frac{\delta P^{(m)}(k')}{\delta G(k)}-mP^{(m)}(k')\frac{\delta W(k')}{\delta G(k)}\right]dk'. \qquad \text{(B13)}$$

The functional derivatives of the mW's in $P^{(m)}$ cancel the last term in Eq. (B13), while the functional derivatives of the $2(m+1)$ explicit G's in $P^{(m)}$ give $-M^{(m+1)}$. A look at the details shows that $W\delta P^{(0)}/\delta G$ would not have given $M^{(1)}$ if we had had normal G's instead of modified G's in $P^{(0)}$. We have actually checked Eq. (B12) only for $n=0$, 1, and 2, but from the structure of the theory we conjecture that Eq. (B12) is valid for arbitrary n.

There are a few comments that can be made in connection with the important Eq. (B12). We note that there is a *definite coupling between $P^{(n)}$ and $M^{(n+1)}$*. We can thus not expand P to say first order and obtain an equation with M also of first order. It is further *not possible to sum just the ladder bubbles of Eq. (61)*. This is clear if we look at $P^{(2)}$, Fig. 2, where there is a mutual cancellation between the W derivatives of the first three diagrams. Each of these gives one third the sum of the first three diagrams in $M^{(3)}$, Fig. 1. The last three diagrams in $P^{(2)}$ on the other hand cancel their W derivatives individually and are in one-to-one correspondence with the last three diagrams of $M^{(3)}$.

So far we only know that the Φ of Eq. (B12) obeys Eq. (B2). We have also to check that Eq. (B1) is satisfied. It is enough to prove that $\lambda(d\Delta E/d\lambda)=\langle V\rangle$ since $\Delta E=0$ for $\lambda=0$. Comparing Eqs. (B12), (B9), and (B1) we see that $\lambda(d/d\lambda)$ applied on the explicit λv of the logarithm in Eq. (B12) gives $\langle V\rangle$. The remaining λ's appear in connection with W and G. It is easy to see by comparing with Eq. (B13) and the discussion following that equation that these terms vanish.

The generalization of the electron-gas results to a nonuniform system is fairly simple. In the general case we have to take account also of the $V(\mathbf{x})$ term of Eq. (7), which vanishes identically for an electron gas in a uniform positive background. Glancing at Eqs. (7), (B1), and (B12) we write

$$\Delta E(G)=-\frac{1}{2}\int d\mathbf{x}d\mathbf{x}'\frac{d\epsilon}{2\pi}\frac{d\epsilon'}{2\pi}e^{i\epsilon\Delta}e^{i\epsilon'\Delta}G(\mathbf{x},\mathbf{x};\epsilon)G(\mathbf{x}',\mathbf{x}';\epsilon')v(\mathbf{x},\mathbf{x}')$$
$$-\frac{i}{2}\int\frac{d\epsilon}{2\pi}\left[\mathrm{Tr}\left(\ln(1-P(\epsilon)v)+W(\epsilon)\sum\frac{n}{n+1}P^{(n)}(\epsilon)\right)\right]+i\int\frac{d\epsilon}{2\pi}e^{i\epsilon\Delta}\,\mathrm{Tr}(G_0^{-1}(\epsilon)G(\epsilon)-1-\ln G_0^{-1}(\epsilon)G(\epsilon)). \qquad \text{(B14)}$$

Here the quantities inside the trace are considered as matrices labelled by $(\mathbf{x},\mathbf{x}')$ where $\mathbf{x}$ includes position and spin. The unperturbed state is taken with full interaction between electrons and nuclei. On account of the cyclical property of a trace we can take derivatives of the matrices as if they were scalars. The proof that Eq. (B14) gives the correct energy shift and the correct equation for G follows similar lines as that for the electron gas.

Equation (B14) is however rather inconvenient since G_0 is very different from G as soon as the nuclear charge Z is larger than, say, 2. It is easy to realize that all occupied functions in G_0 will then be closely the same as those of an ion with charge Z. Thus, e.g., in case of a metal, what must become conduction electrons in G will in G_0 look like tightly bound core electrons. To improve the situation we split the Hamiltonian into an unperturbed part

$$H_0=\int\psi^\dagger(\mathbf{x})h(\mathbf{x})\psi(\mathbf{x})d\mathbf{x}+\int\psi^\dagger(\mathbf{x})V_{\mathrm{eff}}(\mathbf{x},\mathbf{x}')\psi(\mathbf{x}')d\mathbf{x}d\mathbf{x}', \qquad \text{(B15)}$$

and a perturbation

$$H_1=\lambda\left\{\frac{1}{2}\int\psi^\dagger(\mathbf{x})\psi^\dagger(\mathbf{x}')v(\mathbf{x},\mathbf{x}')\psi(\mathbf{x}')\psi(\mathbf{x})d\mathbf{x}d\mathbf{x}' -\int\psi^\dagger(\mathbf{x})V_{\rm eff}(\mathbf{x},\mathbf{x}')\psi(x')d\mathbf{x}d\mathbf{x}' +\tfrac{1}{2}\sum_{nm}{}' Z_nZ_mv(\mathbf{R}_n,\mathbf{R}_m)\right\}. \quad \text{(B16)}$$

$V_{\rm eff}$ can be chosen quite arbitrary but we may think of a Hartree potential plus Coulomb-hole and screened-exchange potentials. The $\Delta E(G)$ corresponding to H_1 of Eq. (16) is given by Eq. (B14) plus two additional terms,

$$\Delta E(G)=\text{Eq. (B14)}+i\int\frac{d\epsilon}{2\pi}e^{i\epsilon\Delta}\,\mathrm{Tr}(V_{\rm eff}G(\epsilon)) +\tfrac{1}{2}\sum_{nm}{}' Z_nZ_mv(\mathbf{R}_n,\mathbf{R}_m). \quad \text{(B17)}$$

The G_0 of Eq. (B14) now of course corresponds to Eq. (B15). It is easily checked that Eq. (B17) gives the correct energy shift and equation for G.

The unperturbed energy corresponding to Eq. (B15) is simply the sum of the N smallest eigenvalues of the one-electron operator $h+V_{\rm eff}$. While this generally is not a good approximation of the true energy, it is on the other hand not very far off. *The importance of the split into H_0+H_1 lies however in the fact that G_0 has now become quite realistic.* Specifically, if we approximate G by G_0 in Eq. (B17) we find that the $V_{\rm eff}\,G$ term cancels against the same term in E_0 and that the last integral in Eq. (B14) vanishes. The GGv term is the Coulomb energy and the $\ln(1-Pv)$ term gives in the lowest approximation the HF exchange energy. If we want, we can gradually improve $V_{\rm eff}$ to make G_0 more closely like G. This is, however, only possible up to a certain point since $V_{\rm eff}$ is energy-independent.

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Cyclotron Resonance in Cadmium

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Extensive observations at 1.5°K and both 23.8 Gc/sec and 74.2 Gc/sec of cyclotron-resonance phenomena in cadmium are reported. One group of experiments is done with the steady applied field parallel to the sample plane (Azbel'-Kaner geometry). A large number of signals are observed, only some of which are sufficiently reliable to identify with cyclotron masses. All the masses are plotted versus the crystallographic orientation of the steady applied field in three of the principal planes. The reliable, well resolved signals are identified and associated tentatively with orbits. Most of these orbits are consistent with the current model of the Fermi surface of cadmium, but some of them require small modifications of it. These orbits are either on the "pillow" or on the large surface associated with holes in the second band. The masses observed with the magnetic field parallel to the sample plane are all too large to identify plausibly with the smaller pieces of the Fermi surface such as the "butterflies" and "cigars". It is suggested that the resonances associated with the charge carriers of smaller mass are lost in the signals from harmonics of those of larger mass. In another group of experiments, data have been obtained with the steady applied field normal to the sample surface. Here signals are obtained at classical cyclotron-resonance fields equal to those observed in the other geometry although the signals are in the anomalous-skin-effect regime and the much larger effects associated with Doppler-shifted cyclotron resonance are at magnetic fields too high to be observed. A theoretical treatment and a discussion of the physics of these effects is given. In this geometry, a cyclotron mass of approximately 0.22 m_0 is also observed. The related orbit is only tentatively identified, but it is definitely thought to involve one of the smaller pieces of the Fermi surface.

I. INTRODUCTION

EXTENSIVE observations of cyclotron resonance in cadmium obtained by plotting the variation of surface absorption coefficient as a function of steady applied magnetic field are presented in this paper and interpreted in terms of current theoretical understanding of the Fermi surface. The experimental results given here extend previously reported preliminary studies on this metal.[1] Data were obtained at 1.5°K at frequencies near both 23.8 Gc/sec and 74.2 Gc/sec. Most of the data were obtained at various crystallographic orientations with the steady applied magnetic field parallel to the plane sample surface, i.e., in the Azbel'-Kaner geometry.[2] From these data, plots of cyclotron masses as a function of crystallographic orientation were made. In addition, data have been obtained for selected crystallographic orientations with the steady applied field normal to the plane sample

[1] J. K. Galt, F. R. Merritt, and P. H. Schmidt, Phys. Rev. Letters **6**, 458 (1961).

[2] M. Ya Azbel' and E. A. Kaner, Zh. Eksperim. i Teor. Fiz. **30**, 811 (1956) [English transl.: Soviet Phys.—JETP **3**, 772 (1956)]; J. Phys. Chem. Solids **6**, 113 (1958).