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Polarization of the Electron Gas in Metals by Substitutional Impurities*

B. D. SILVERMAN†‡ AND P. R. WEISS
Physics Department, Rutgers University, New Brunswick, New Jersey

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The ground-state energy of the system of impurities and conduction electrons in a metal has been obtained in the high electron density limit. The procedure used is an extension of the Wentzel method applied to a reduced Hamiltonian which includes an electron-impurity interaction. It is reduced in the sense that the Coulomb interaction between electrons and the electron-impurity interaction are only effective in raising an electron in a state below the Fermi level to one above and vice versa. The ground-state energy is then obtained by a canonical transformation. The shift in energy of the ground state of the electron gas, due to the introduction of the impurities, is quadratic in the electron-impurity matrix element. Higher order processes in this matrix element do not contribute since they are represented by unlinked diagrams. Considering this shift in the ground-state energy expandable in powers of r_s, a measure of the average interelectronic distance, we show the leading or lowest order term in this parameter to go as $(n/n_e)r_s^{-\frac{1}{2}}$, where n is the impurity density and n_e the electron density. Impurity locations are assumed random. All processes omitted in the reduction of the Hamiltonian are shown to contribute to higher powers in r_s. The role of exchange is indicated.

I. INTRODUCTION

WE consider the shift in the ground-state energy of a metal due to the polarization of the free electrons by substitutional impurities. For this purpose we use a highly simplified model of a metal in which the positively charged ions are smeared out and thereby eliminate complications due to band structure. The impurities are represented by point charges whose magnitude is determined by the valence of the impurity with respect to that of the host atom. In this model the impurity charges destroy the uniformity of the electron density distribution causing a local bunching of the electrons in their neighborhood. This change from a uniform distribution is what we have labeled the polarization of the electrons. This local bunching serves to shield the impurities and also to change the energy of the system.

In Sec. II the ground-state energy of the system is obtained by performing a canonical transformation on a reduced Hamiltonian. The Hamiltonian is reduced in the sense that electron-electron and electron-impurity interaction matrix elements connecting only states below the Fermi level with those above are included. There are two contributions to the ground-state energy of the system. One is just that calculated by Wentzel[1] for the electron gas proper without impurities. The second contribution is the shift in the ground-state energy of the electron gas due to the introduction of the impurities. This energy shift we find to be quadratic in the electron-impurity matrix element. With the restrictions in the matrix elements noted above, no higher order terms appear. This means that only when matrix elements of the electron-impurity interaction which connect states above the Fermi level are included will terms of higher order in this interaction appear in the ground-state energy. We do not include such terms since in Sec. VI we show that such terms are negligible in the high electron density limit.

In Sec. III we show the shift in energy as calculated by a self-consistent Hartree field procedure is the same as that given by the canonical transformation. This shift in energy arises from three sources. One is the change in kinetic energy of the electrons. The second is the interaction of the impurities with the electron bunching. Lastly there is the change in electron-electron interaction energy due to the bunching. We emphasize that the Hartree method does not yield the correct energy in the absence of the impurities.

In Sec. IV we discuss the calculation of the shift in the ground-state energy to second order in the electron-electron interaction matrix element in terms of a formal perturbation expansion and compare this with the result of the canonical transformation. The two approaches agree to the order calculated. Terms in the perturbation expansion which include more than two powers of the above to below (or vice versa) electron-impurity interaction lead to unlinked diagrams and so do not contribute to the energy.[2]

In Sec. V we evaluate the change in energy. We find the shift in energy per electron to vary as $(n/n_e)r_s^{-\frac{1}{2}}$, where n is the number density of impurities, n_e the number density of electrons and r_s is a measure of the interelectronic spacing. In Sec. VI we show the shift in energy to be exact in the high electron density limit by an examination of the equations of motion for the electron density fluctuations. Since the Wentzel result for the electron gas proper is also a high electron density calculation, the total result for the ground-state energy inclusive of impurities is also exact in the limit of high density. In conclusion we indicate the role played by exchange.

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† Now at the Research Division, Raytheon Mfg. Company, Waltham, Massachusetts.

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[1] G. Wentzel, Phys. Rev. **108**, 1593 (1957).

[2] J. Goldstone, Proc. Roy. Soc. (London) **A239**, 267 (1957).

II. CANONICAL TRANSFORMATION

Gell-Mann and Brueckner[3] develop the energy of the ground state of an electron gas in a perturbation series expansion. The kinetic energy of the electrons is considered to be the unperturbed part of the Hamiltonian and the Coulomb interaction energy between electrons is considered the perturbation. The unperturbed energy is just that for a system of N noninteracting electrons. The first-order correction is due to exchange. The nonexchange first-order contribution to the energy is canceled against the contribution to the energy from the smeared-out lattice. The second- and higher-order contributions diverge. Gell-Mann and Brueckner meet this difficulty by summing all order processes in which electrons hand the same momentum on successively to others before falling back into the Fermi sea. It is only these processes which contribute to the ground-state energy in the high density limit. Other processes such as the scattering of electrons above the Fermi level become important at lower densities; that is to say, they contribute to terms in the energy of higher order in r_s.

$$r_s=\frac{r_0}{a_0};\quad \frac{\Omega}{\frac{4}{3}\pi r_0^3}=N, \tag{2.1}$$

where a_0 is the Bohr radius and Ω is the normalization volume.

The energy of the system is written in powers of r_s. The Gell-Mann—Brueckner procedure is an exact calculation of the constant term in this series. The unperturbed energy or kinetic energy of the electrons goes as r_s^{-2} and the exchange contribution as r_s^{-1}.

Sawada[4] writes a Hamiltonian in the language of second quantization which includes a reduced Coulomb interaction between electrons. This reduced interaction includes no exchange interaction of excited electrons, no exchange interactions of holes and no interactions with an odd number of creation operators. The ground-state energy is then obtained by a procedure similar to that introduced by Wentzel.[5] The result is the same as that obtained by Gell-Mann and Brueckner. In a subsequent paper Wentzel[1] shows how an effective kinetic energy operator may be defined for the electrons so that the ground-state energy may be solved for in a manner formally equivalent to that described in his earlier paper. This is a simplification of the Sawada procedure.

We will add the interaction between the impurities and electrons to the Sawada Hamiltonian. This interaction will be reduced in a manner we will describe. The Hamiltonian will then be written in the Wentzel coordinates and transformed to normal form by a canonical transformation.

Sawada writes the Hamiltonian

$$\begin{aligned}H_s=H_0+H_c=&\sum_{\mathbf{k}} E_{\mathbf{k}}A_{\mathbf{k}}^*A_{\mathbf{k}}+\sum_{\mathbf{k}+\mathbf{q}} E_{\mathbf{k}+\mathbf{q}}A_{\mathbf{k}+\mathbf{q}}^*A_{\mathbf{k}+\mathbf{q}}\\&+\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}}\lambda_{\mathbf{q}}(A_{\mathbf{k}+\mathbf{q}}^*A_{\mathbf{k}}+A_{\mathbf{k}}^*A_{\mathbf{k}-\mathbf{q}})\\&\times(A_{\mathbf{k}'-\mathbf{q}}^*A_{\mathbf{k}'}+A_{\mathbf{k}'}^*A_{\mathbf{k}'+\mathbf{q}}),\end{aligned} \tag{2.2}$$

where $|\mathbf{k}+\mathbf{q}|>k_F$; $|\mathbf{k}|<k_F$, $\lambda_q=4\pi e^2/\Omega q^2$. The $A_{\mathbf{k}}$ and $A_{\mathbf{k}}^*$ are the usual destruction and creation operators. The electron-impurity interaction is written

$$H_i=\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{q}} V_{\mathbf{q}}^iA_{\mathbf{k}}^*A_{\mathbf{k}+\mathbf{q}}+\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{q}} V_{-\mathbf{q}}^iA_{-\mathbf{k}}^*A_{-\mathbf{k}-\mathbf{q}}, \tag{2.3}$$

where $V_{\mathbf{q}}^i$ is the qth Fourier component of the electron-impurity potential.

The above sums are over all $\mathbf{k}$ and $\mathbf{q}$. To be able to make the transition to Wentzel's notation we must restrict the interaction to give rise to those virtual processes in which electrons below the Fermi level are raised above and those above are returned below. Imposing this restriction we may write

$$H_i=\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{q}}[V_{\mathbf{q}}^i\{A_{\mathbf{k}}^*A_{\mathbf{k}+\mathbf{q}}+(A_{-\mathbf{k}}^*A_{-\mathbf{k}-\mathbf{q}})^*\}+\text{c.c.}]. \tag{2.4}$$

The total Hamiltonian of the system may be written

$$H=H_s+H_i. \tag{2.5}$$

At this step the effective kinetic energy operator of Wentzel is introduced and the Hamiltonian is written in the Wentzel coordinates

$$\begin{aligned}\varphi_{\mathbf{k},\mathbf{q}}&=\varphi_{-\mathbf{k},-\mathbf{q}}^*=\frac{1}{(2\omega_{\mathbf{k},\mathbf{q}})^{\frac{1}{2}}}(C_{\mathbf{k},\mathbf{q}}+C_{-\mathbf{k},-\mathbf{q}}^*),\\ \pi_{\mathbf{k},\mathbf{q}}&=\pi_{-\mathbf{k},-\mathbf{q}}^*=i\left(\frac{\omega_{\mathbf{k},\mathbf{q}}}{2}\right)^{\frac{1}{2}}(C_{\mathbf{k},\mathbf{q}}^*-C_{-\mathbf{k},-\mathbf{q}}),\end{aligned} \tag{2.6}$$

where

$$C_{\mathbf{k},\mathbf{q}}=A_{\mathbf{k}}^*A_{\mathbf{k}+\mathbf{q}};\quad \omega_{\mathbf{k},\mathbf{q}}=E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}},$$

$$\begin{aligned}H=&\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{q}}(\pi_{\mathbf{k},\mathbf{q}}^*\pi_{\mathbf{k},\mathbf{q}}+\omega_{\mathbf{k},\mathbf{q}}^2\varphi_{\mathbf{k},\mathbf{q}}^*\varphi_{\mathbf{k},\mathbf{q}}-\omega_{\mathbf{k},\mathbf{q}})\\&+\sum_{\mathbf{q}}\lambda_{\mathbf{q}}(\sum_{\mathbf{k}}\omega_{\mathbf{k},\mathbf{q}}^{\frac{1}{2}}\varphi_{\mathbf{k},\mathbf{q}}^*)(\sum\omega_{\mathbf{k}'\mathbf{q}}^{\frac{1}{2}}\varphi_{\mathbf{k}'\mathbf{q}})\\&+\tfrac{1}{2}\sum_{\mathbf{k},\mathbf{q}}(2\omega_{\mathbf{k},\mathbf{q}})^{\frac{1}{2}}(V_{\mathbf{q}}^i\varphi_{\mathbf{k},\mathbf{q}}+\text{c.c.}).\end{aligned} \tag{2.7}$$

This Hamiltonian may be diagonalized by transforming to a new set of coordinates, the origins of which are displaced with respect to those of the old coordinates. The new coordinates Q, P are related to the old coordi-

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[3] M. Gell-Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957).
[4] K. Sawada, Phys. Rev. **106**, 372 (1957).
[5] G. Wentzel, Helv. Phys. Acta **15**, 111 (1942).

nates φ, π by the relations

$$\varphi_{\mathbf{k}}=\sum_{\mathbf{k}'} d_{\mathbf{k}\mathbf{k}'}Q_{\mathbf{k}'}+b_{\mathbf{k}},$$

$$\pi_{\mathbf{k}}=\sum_{\mathbf{k}'} d_{\mathbf{k}\mathbf{k}'}{}^{*}P_{\mathbf{k}'}, \qquad (2.8)$$

where the $d_{\mathbf{k}\mathbf{k}'}$ and the $b_{\mathbf{k}}$ are constants and satisfy the relations

$$\delta_{\mathbf{k},\,\mathbf{k}'}=\sum_{\mathbf{k}''} d_{\mathbf{k}\mathbf{k}''}d_{\mathbf{k}'\mathbf{k}''}{}^{*};\quad \sum_{\mathbf{k}} \omega_{\mathbf{k}}{}^{\frac{1}{2}}b_{\mathbf{k}} =-\frac{2^{\frac{1}{2}}V_{\mathbf{q}}{}^{i*}\sum_{\mathbf{k}} 1/\omega_{\mathbf{k},\,\mathbf{q}}}{1+2\lambda_{q}\sum_{\mathbf{k}} 1/\omega_{\mathbf{k},\,\mathbf{q}}}. \qquad (2.9)$$

The $b_{\mathbf{k}}$ are determined in this way in order to eliminate terms linear in Q. After the transformation the Hamiltonian is written as

$$H=\tfrac{1}{2}\sum_{\mathbf{k},\,\mathbf{q}} (P_{\mathbf{k},\,\mathbf{q}}{}^{*}P_{\mathbf{k},\,\mathbf{q}}+\Omega_{\mathbf{k},\,\mathbf{q}}{}^{2}Q_{\mathbf{k},\,\mathbf{q}}{}^{*}Q_{\mathbf{k},\,\mathbf{q}}-\omega_{\mathbf{k},\,\mathbf{q}}) -\sum_{\mathbf{q}} \frac{|V_{q}{}^{i}|^{2}T}{(1+2\lambda_{q}T)}, \qquad (2.10)$$

where $T=\sum_{|\mathbf{k}|<k_F} 1/\omega_{\mathbf{k},\,\mathbf{q}}$.

The second term on the right, is the shift in the ground-state energy due to the introduction of the impurities. The same result can be obtained by the self-consistent Hartree field or a Nakajima type procedure. The first term on the right gives the high density ground-state energy of the electron gas without impurities. The exchange term $\epsilon_b{}^2$ must be added to this result (see Gell-Mann and Brueckner[3]). The $\Omega_{\mathbf{k},\,\mathbf{q}}$ satisfy the dispersion relation as derived by Wentzel. We again make note of the fact that the shift in the ground-state energy is quadratic in the electron-impurity matrix element. It should also be remarked that the *change* in electron density due to the introduction of the impurities as calculated by this method is the same as that derived from the self-consistent field calculation.

III. SELF-CONSISTENT HARTREE FIELD[6]

We perform a one-electron perturbation calculation with the Hamiltonian

$$(H_0+V)\psi=E\psi, \qquad (3.1)$$

where H_0 is the kinetic energy operator for a given electron and V is the potential experienced by the electron. V will be treated as a perturbation. In the absence of the potential V, the wave function for an electron of momentum $\hbar\mathbf{k}$ is just

$$\psi_{\mathbf{k}}{}^{0}=\frac{1}{\Omega^{\frac{1}{2}}}\exp(i\mathbf{k}\cdot\mathbf{r}), \qquad (3.2)$$

where Ω is the normalization volume and $\psi_{\mathbf{k}}{}^{0}$ satisfies

$$H_0\psi_{\mathbf{k}}{}^{0}=E_{\mathbf{k}}{}^{0}\psi_{\mathbf{k}}{}^{0}. \qquad (3.3)$$

The first order correction to the wave function may be written

$$\psi_{\mathbf{k}}=\psi_{\mathbf{k}}{}^{0}+\frac{1}{(E_0-H_0)}(V-E_1)\psi_{\mathbf{k}}{}^{0};$$

$$E_1=\int \psi_{\mathbf{k}}{}^{0*}V\psi_{\mathbf{k}}{}^{0}d\tau, \qquad (3.4)$$

and expanding $V\psi_{\mathbf{k}}{}^{0}$ in plane waves we may write

$$\psi_{\mathbf{k}}=\psi_{\mathbf{k}}{}^{0}+\sum_{\mathbf{q}} \frac{V_{\mathbf{q}}}{(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}})}\psi_{\mathbf{k}+\mathbf{q}}{}^{0}. \qquad (3.5)$$

We now impose the self-consistency requirement that the potential an electron experiences is determined by the charge density through Poisson's equation

$$\nabla^2 V^e=-4\pi e\rho;\quad V=V^e+V^i, \qquad (3.6)$$

where V^e is the potential an electron experiences due to the other electrons and V^i that due to the test charges.

The change in electron density at any point due to introduction of the impurities $\mathbf{R}_j$ may be written

$$\rho=e\sum_{|\mathbf{k}|<k_F} (\psi_{\mathbf{k}}{}^{*}\psi_{\mathbf{k}}-\psi_{\mathbf{k}}{}^{0*}\psi_{\mathbf{k}}{}^{0}) =2e\sum_{\mathbf{k},\,\mathbf{q}} \frac{V_{\mathbf{q}}}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}\frac{\exp(i\mathbf{q}\cdot\mathbf{r})}{\Omega}. \qquad (3.7)$$

$\mathbf{R}_j$ is any impurity location. Expanding V^e in plane waves and using (3.6) we get

$$q^2V_{\mathbf{q}}{}^{e}=\frac{4\pi e^2}{\Omega}V_{\mathbf{q}}\sum_{\mathbf{k}} \frac{1}{E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}}}. \qquad (3.8)$$

From the Fourier transform of (3.6) and the use of (3.8) we get

$$V_q=V_{q}{}^{i}\bigg/\left(1+2\lambda_q\sum_{|\mathbf{k}|<k_F} \frac{1}{E_{\mathbf{k}+\mathbf{q}}-E_{\mathbf{k}}}\right). \qquad (3.9)$$

Note that the impurity potential is screened; this is the meaning of the second term in the denominator.

We now calculate the change in energy of the system from the energy of the system before the point charges are added. There are three contributions to this change in energy. One arises from the change in kinetic energy of the electrons. Another results from the interaction of the impurities with the electron bunching. The third is the change in the electron-electron interaction energy of the system due to the bunching.

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[6] P. R. Weiss, Lectures in Theoretical Solid State, 1957 (unpublished); J. Quinn and R. Ferrell, Bull. Am. Phys. Soc. Ser. II, 3, 53 (1958); J. Bardeen, Phys. Rev. 52, 688 (1937).

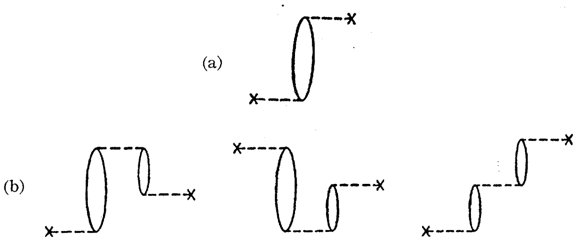

FIG. 1. (a) Processes contributing to the energy from the zeroth order electron-electron interaction. (b) Process contributing to the energy from the first-order electron-electron interaction.

These may be written

$$\Delta E_K=\sum_{|\mathbf{k}|<k_F}\frac{\int \psi_{\mathbf{k}}{}^* H_0 \psi_{\mathbf{k}} d\tau-\int \psi_{\mathbf{k}}{}^{0*} H_0 \psi_{\mathbf{k}}{}^0 d\tau}{\int \psi_{\mathbf{k}}{}^* \psi_{\mathbf{k}} d\tau}=\sum_{\mathbf{q}}\frac{|V_{\mathbf{q}}{}^i|^2 T}{(1+2\lambda_q T)^2}, \tag{3.10}$$

$$\Delta E_i=-\sum_j \int \frac{ze\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_j|}d\tau=-2\sum_{\mathbf{q}}\frac{|V_{\mathbf{q}}{}^i|^2 T}{(1+2\lambda_q T)}, \tag{3.11}$$

$$\Delta E_0=\tfrac{1}{2}\int\int\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\tau d\tau'=2\sum_{\mathbf{q}}\frac{\lambda_q |V_{\mathbf{q}}{}^i|^2 T^2}{(1+2\lambda_{\mathbf{q}} T)^2}, \tag{3.12}$$

where z is the impurity charge above that of the host ion.

For the total change we obtain

$$\Delta E=\Delta E_K+\Delta E_i+\Delta E_c =-\sum\nolimits_{\mathbf{q}} |V_{\mathbf{q}}{}^i|^2 T/(1+2\lambda_q T). \tag{3.13}$$

IV. PERTURBATION EXPANSION

An alternative procedure is to consider the electron-electron and electron-impurity interactions as perturbations and to use a formal perturbation theory. The nth order correction to the energy may be written[7] as

$$E_n=\left\langle \psi_0 \left| (H_c+H_i)\left\{\frac{P}{(H_0-E_0)}(H_c+H_i)\right\}^{n-1}\right| \psi_0\right\rangle, \tag{4.1}$$

where P designates the taking of a principal value and only contributions from linked diagrams are included. We have to go from ground state to ground state by way of intermediate states. Three kinds of terms appear in the perturbation expansion. There are terms which include only processes by way of H_c, terms which include only processes by way of H_i, and terms which include processes due to a mixture of both H_c and H_i. A certain subset of those terms containing only powers of H_c give rise to the first term in Eq. (2.10). This is just the Wentzel result. There are no terms containing only a single power of H_i. This is so since the ground state could not be reached again. Terms in the second power of H_i are of two types; in the first each H_i connects states below the Fermi level with those above. The second type includes other possibilities. We have calculated the contributions of the first type out to the second power in H_c.

We expand the energy shift from Eq. (2.10) to second power in H_c.

$$-\sum_{\mathbf{q}}\frac{|V_{\mathbf{q}}{}^i|^2 T}{(1+2\lambda_q T)}=-\sum_{\mathbf{q}}|V_{\mathbf{q}}{}^i|^2 T+2\sum_{\mathbf{q}}\lambda_q |V_{\mathbf{q}}{}^i|^2 T^2 -4\sum_{\mathbf{q}}\lambda_q{}^2 |V_{\mathbf{q}}{}^i|^2 T^3+\cdots. \tag{4.2}$$

The contribution from the zeroth order Coulomb interaction may be written down immediately

$$-\left\langle \psi_0 \left| \sum_{\mathbf{k},\mathbf{q}} |V_{\mathbf{q}}{}^i|^2 A_{\mathbf{k}}{}^* A_{\mathbf{k}+\mathbf{q}} \frac{1}{(H_0-E_0)} A_{\mathbf{k}+\mathbf{q}}{}^* A_{\mathbf{k}} \right| \psi_0 \right\rangle =-\sum_{\mathbf{q}} |V_{\mathbf{q}}{}^i|^2 T. \tag{4.3}$$

This is illustrated diagrammatically in Fig. 1(a). Processes contributing to the first order in the Coulomb interaction matrix element are illustrated in Fig. 1(b). A cross at the end of a dashed line represents the scattering of an electron from below the Fermi level to above or vice versa via the electron-impurity interaction. A dashed line without a cross represents the Coulomb scattering of two electrons from below the Fermi level to above or vice versa. Those processes contributing to the energy to second order in the electron-electron Coulomb interaction matrix element are not illustrated in Fig. 1. There are eighteen such terms and we have summed them all. The result is precisely the third term on the right of Eq. (4.2). The higher order terms in H_c have not been evaluated but we feel confident that they also will agree with the corresponding terms in Eq. (4.2).

Goldstone[2] has shown in general that all order contributions to the energy arising from unlinked diagrams are zero. The reason that the shift in energy is quadratic in the electron-impurity matrix element is that all higher order processes in this matrix element considered in the treatment of Sec. II are unlinked. A few of these processes are illustrated in Fig. 2.

V. CHANGE IN THE GROUND-STATE ENERGY

We will evaluate

$$\Delta E=-\sum_{\mathbf{q}}\frac{|V_{\mathbf{q}}{}^i|^2 T}{(1+2\lambda_q T)}=-\frac{\Omega}{8\pi^3}\int\frac{|V_{\mathbf{q}}{}^i|^2 T d\mathbf{q}}{(1+2\lambda_q T)}, \tag{5.1}$$

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[7] W. Kohn, Phys. Rev. **110**, 857 (1958).

where

$$T=\sum_{\mathbf{k}}\frac{1}{\omega_{\mathbf{k},\,\mathbf{q}}}=\frac{4m}{\hbar^2}\frac{\Omega}{8\pi^3}\int\frac{d\mathbf{k}}{(\mathbf{k}+\mathbf{q})^2-k^2}$$

$$=\frac{4m}{\hbar^2}\frac{\Omega}{16\pi^2 q}\left[qk_F-(k_F{}^2-q_4{}^2)\ln\left|\frac{q_2-k_F}{q_2+k_F}\right|\right]. \quad (5.2)$$

This integration (5.2) can be performed most easily by making use of cylindrical coordinates.

We consider impurity locations distributed randomly and average over them in a suitable manner.[8] The result of this averaging yields

$$|V_{\mathbf{q}}{}^i|^2=\frac{16\pi^2z^2e^4n}{\Omega q^4}, \quad (5.3)$$

where n is the number density of impurities. Using (5.3) in (5.1) one can calculate the energy density. An examination of the integral shows that as the electron density is increased, the major contribution to this energy shift comes from smaller and smaller $\mathbf{q}$ values (with respect to k_F). That is, in the high-density limit only the long-range response of the system is important.

We have integrated Eq. (5.1) by an expansion of the logarithm and find in the high-density limit

$$\Delta E=-\frac{2z^2}{\pi^{\frac{1}{2}}}\frac{1}{\alpha^{\frac{1}{2}}}\frac{n}{n_e}r_s{}^{-\frac{1}{2}}, \quad (5.4)$$

where $\alpha=(4/9\pi)^{\frac{1}{3}}$. Equation (5.4) is the energy shift per particle in Rydberg units. The screened impurity potential is obtained by considering

$$V_{\mathbf{q}}=\frac{V_{\mathbf{q}}{}^i}{(1+2\lambda_q T)}. \quad (5.5)$$

We again expand the logarithm and take the Fourier transform of $V_{\mathbf{q}}$ to obtain the screened one-electron impurity potential. The result is

$$V(\mathbf{r})=-\sum_j\frac{ze^2}{|\mathbf{r}-\mathbf{R}_j|}e^{-k_s|\mathbf{r}-\mathbf{R}_j|}, \quad (5.6)$$

where $k_s{}^2=4k_F/\pi a_0$.

VI. HIGH ELECTRON DENSITY LIMIT—EXCHANGE

First we show that the behavior of the system in the limit of high electron density is completely described by virtual processes connecting only states below the Fermi level with those above.

From the Hamiltonian

$$H=\sum_j\frac{P_j{}^2}{2m}+\tfrac{1}{2}\sum_{\mathbf{q}}{}'\lambda_q\rho_{\mathbf{q}}\rho_{-\mathbf{q}}-\sum_{\mathbf{q}}{}'\lambda_q\rho_{-\mathbf{q}}r_{\mathbf{q}}, \quad (6.1)$$

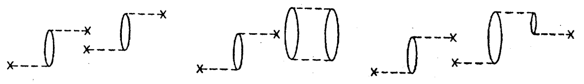

FIG. 2. Unlinked diagrams.

where

$$\rho_{\mathbf{q}}=\textstyle\sum_j e^{-i\mathbf{q}\,\mathbf{r}_j}; \quad r_{\mathbf{q}}=z\textstyle\sum_j e^{-i\mathbf{q}\,\mathbf{R}_j},$$

we get for the equation of motion for the qth density fluctuation

$$\frac{d^2\rho_{\mathbf{q}}}{dt^2}=-\sum_j\left\{\frac{\mathbf{q}}{m}\cdot\left(P_j+\frac{\hbar\mathbf{q}}{2}\right)\right\}^2e^{-i\mathbf{q}\cdot\mathbf{r}_j}$$

$$-\sum_{\mathbf{q}'}{}'\lambda_{q'}\frac{\mathbf{q}\cdot\mathbf{q}'}{m}\rho_{\mathbf{q}'}\sum_j e^{i(\mathbf{q}'-\mathbf{q})\cdot\mathbf{r}_j}$$

$$+\sum_{\mathbf{q}'}{}'\lambda_{q'}\frac{\mathbf{q}\cdot\mathbf{q}'}{m}r_{\mathbf{q}'}\sum_j e^{i(\mathbf{q}'-\mathbf{q})\cdot\mathbf{r}_j}. \quad (6.2)$$

Primes indicate that the $\mathbf{q}'=0$ term is excluded from the summation. The first term on the right is the electron thermal motion contribution to $d^2\rho_{\mathbf{q}}/dt^2$. The second and third terms arise, respectively, from the electron-electron and electron-impurity interaction. From these two terms we separate out the terms for which $\mathbf{q}'=\mathbf{q}$ and transpose them to the left side of the equation. We get

$$\frac{d^2\rho_{\mathbf{q}}}{dt^2}+\omega^2(\rho_{\mathbf{q}}-\rho_{\mathbf{q}}{}^0)=-\sum_j\left\{\frac{\mathbf{q}}{m}\cdot\left(P_j+\frac{\hbar\mathbf{q}}{2}\right)\right\}^2e^{-i\mathbf{q}\cdot\mathbf{r}_j}$$

$$-\sum_{\mathbf{q}'\neq\mathbf{q}}\lambda_{q'}\frac{\mathbf{q}\cdot\mathbf{q}'}{m}\rho_{\mathbf{q}}{}'\rho_{\mathbf{q}-\mathbf{q}'}$$

$$+\sum_{\mathbf{q}'\neq\mathbf{q}}\lambda_{q'}\frac{\mathbf{q}\cdot\mathbf{q}'}{m}r_{\mathbf{q}'}\rho_{\mathbf{q}-\mathbf{q}'}, \quad (6.3)$$

where

$$\omega^2=\frac{4\pi n_e e^2}{m}; \quad \rho_{\mathbf{q}}{}^0=r_{\mathbf{q}}.$$

In the high electron density limit an analysis similar to that by Bohm and Pines[9] shows the terms on the right of Eq. (6.3) small compared with those on the left. We see that the impurities just shift the zero of each density fluctuation by the amount $r_{\mathbf{q}}$. Evaluating changes in the electron density by the procedure in Sec. II yields in the high electron density limit

$$q\text{th Fourier component of } \Delta(\psi^*\psi)=r_{\mathbf{q}}. \quad (6.4)$$

The shift in the zero of the density fluctuation shows up as a change in electron density. Fluctuations about the shift average out. We therefore see that the high electron density response of the system to the impurities

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[8] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).

[9] D. Bohm and D. Pines, Phys. Rev. **85**, 338 (1952).

is determined solely by processes included in the treatment of Sec. II. Processes connecting states above the Fermi level therefore contribute to higher powers in r_s than $r_s^{\frac{5}{2}}$ in the expansion of the ground-state energy shift.

Gell-Mann and Brueckner consider the ground-state energy of the electron gas as expanded in powers of the dimensionless parameter r_s. The expansion of the ground-state energy of the electron gas with impurities must be considered to contain another dimensionless parameter, i.e., the ratio of the impurity density to electron density. We define this ratio as

$$R=n/n_e. \tag{6.5}$$

In Sec. V we showed the leading term of the energy shift to go as $Rr_s^{-\frac{1}{2}}$. We are able to establish from an analysis of terms in the perturbation expansion discussed in Sec. IV that all higher order terms not explicitly evaluated there make contributions to this same order in r_s. This is proved as follows. Each term in the perturbation expansion included in the treatment of Sec. II is considered written as a constant multiplied by an integration over dimensionless vectors. The constant involves R multiplied by some power of r_s. In the Gell-Mann and Brueckner calculation the second order electron-electron interaction contribution to the ground-state energy is written as r_s^0 multiplied by an integral over dimensionless vectors. The third order contribution is written as r_s multiplied by an integral over dimensionless vectors and so on. It is easily verified that the second order contribution to the shift in ground state energy can be written as Rr_s^0 multiplied by an integral over dimensionless vectors. The integration over the dimensionless vectors gives rise to the divergence $\lim_{q\to 0}(1/q)$. For the higher orders we have

$$\text{3rd order}\quad Rr_s\frac{1}{q^3}\ \text{divergence},$$

$$\text{4th order}\quad Rr_s^2\frac{1}{q^5}\ \text{divergence},$$

$$\text{5th order}\quad Rr_s^3\frac{1}{q^7}\ \text{divergence},$$

$$\begin{matrix} \vdots & \qquad & \vdots \end{matrix}$$

We see that the sum of such terms will contribute at most to the $Rr_s^{-\frac{1}{2}}$ dependence as calculated in Sec. V if the electron-impurity and electron-electron interactions are cut off at $q_c\sim r_s^{\frac{1}{2}}$. This is just the electron-electron interaction momentum transfer cutoff as calculated by Bohm and Pines.[10]

An exchange interaction in any order reduces the divergence by a factor of q^2. Therefore one exchange interaction in third order gives rise to a divergent term $Rr_s(1/q)$ and therefore contributes at most to the $Rr_s^{\frac{1}{2}}$ dependence in the series expansion. The same may be said for all other higher order processes involving one exchange interaction. We see that as for contributions from diagrams not including an electron-impurity interaction, exchange contributions increase in importance as the density of the electron gas is decreased.[11]

We should also remark that ΔE as calculated by the collective method[12] is

$$\Delta E=-\sum_{|\mathbf{q}|<q_c}\frac{|V_{\mathbf{q}}^i|^2T}{(1+2\lambda_qT)}-\sum_{|\mathbf{q}|>q_c}|V_{\mathbf{q}}^i|^2T,$$

where q_c is the collective momentum transfer cutoff. In the high-density limit this result is the same as we calculate since $q_c\to\infty$.

Note: q_c (dimensionless) $=q_c/k_F\sim r_s^{\frac{1}{2}}$; $k_F\sim 1/r_s$.

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[11] P. Nozières and D. Pines, Phys. Rev. **111**, 442 (1958).
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