Spin Paramagnetism of an Electron Gas in a Lattice of Positive Charges

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The spin paramagnetism of an electron gas in a lattice of positive charges is studied along the line of Bellemans and De Leener. The results are compared with Pines' and also with experimental data on Li and Na.

§ 1. Introduction

Bellemans and De Leener\(^1\)} have studied the ground state energy of an electron gas moving in a lattice of positive charges. This picture is expected to correspond roughly to actual metals or metallic solutions. The purpose of this paper is to extend their treatment to a study of spin paramagnetism.

The magnetic susceptibility of the system is determined by the change in energy as the electron spins are polarized. Let us denote the number of electrons with spin up and down by \( N_+ \) and \( N_- \), and introduce a parameter \( p \):

\[
N_+ = N(1 + p)/2, \quad N_- = N(1 - p)/2,
\]

where \( N \) is the total number of electrons. The Fermi momentum in the polarized system is

\[
k_{\pm} = (1 + p)^{1/2} k_F, \quad k_{\mp} = (1 - p)^{1/2} k_F,
\]

with \( k_F \) the Fermi momentum in the unpolarized system given by \((3\pi^2 n)^{1/3}\) where \( n \) is the number density of electrons.\(^3\)} The change in energy per electron to the lowest order in \( p \) is

\[
\varepsilon(p) - \varepsilon(0) = \alpha p^2/4.
\]

With the Bellemans and De Leener approximation, the energy of the system consists of two parts; one corresponding to an electron gas in a uniform positive charge background, and the other arising from an interaction between electrons and a lattice of positive charges. Therefore \( \alpha \) is expressed as

\[
\alpha = \alpha_p + \alpha_{ex} + \alpha_e + \alpha_L,
\]

\(^3\)} We adopt the following unit system: \( \hbar = 2m = e^2/2 = 1 \), where \( e \) is the electronic charge. Then energies are expressed in Rydberg \( me^4/2\hbar^2 \) and distances in Bohr radius \( \hbar^2/me^2 \).
where $\alpha_p$, $\alpha_{ex}$ and $\alpha_c$ are due to the change in kinetic, exchange and correlation energy of the electron gas in the uniform charge background, and are given by
\begin{align}
\alpha_p &= 4.91/r_s^3, \\
\alpha_{ex} &= -0.814/r_s, \\
\alpha_c &= 0.225 - 0.0676 \ln r_s, 
\end{align}
with $r_s$ defined by $n^{-1} = 4\pi r_s^3/3$. Equation (7) for $\alpha_c$ was derived by Brueckner and Sawada and is exact at a high density limit. The quantity $\alpha_L$ arises from the interaction between electrons and lattice potentials, and was missing in previous treatments of electron gas where positive charges are smeared out.

In § 2 we derive an expression for $\alpha_L$ based on the second order perturbation calculation, and the results are applied to alkali metals in § 3. Section 4 is devoted to some discussions of the results.

## § 2. Calculation of $\alpha_L$

Let us denote a lattice potential acting on an electron by $U(x)$. Since $U(x)$ has the same periodicity as that of lattice, it is expanded as follows:
\begin{equation}
U(x) = \sum_K U(K) \exp(iK \cdot x),
\end{equation}
where $K$ is a reciprocal lattice vector. In the second-quantized form, the hamiltonian $H_{e-L}$ describing the interaction between electrons and lattice potentials is written as
\begin{equation}
H_{e-L} = \sum_{K,k} \psi^*(x) U(K) \psi(x) dx = \sum_{K,k} U(K) a_k^\pi a_k^\pi,
\end{equation}
where $a_k^\pi$ and $a_k$ are creation and annihilation operators for electrons.

The first order term for energy is $U(0) N$, so that it does not contribute to $\alpha_L$. The second order term is
\begin{equation}
E_{L(2)} = \sum_{K,k} |U(K)|^2 \frac{n_\sigma(k) (1 - n_\sigma(k + K))}{k - (k + K)^2},
\end{equation}
where $\sigma$ stands for $+$ or $-$, and $n_\sigma(k) = 1$ for $k < k_\sigma$, and $n_\sigma(k) = 0$ for $k > k_\sigma$. By a straightforward calculation, the energy per electron in the polarized state is shown to be
\begin{equation}
\varepsilon_L(p) = -\frac{r_s^2}{4(2\pi)^3} \sum_{K} |U(K)|^2 \left( (1 + p)^{1/3} f(u_+) + (1 - p)^{1/3} f(u_-) \right),
\end{equation}
where
\begin{equation}
f(u) = 1 + \frac{1 - u^2}{2u} \ln \frac{1 + u}{1 - u},
\end{equation}
and
In the case of metallic hydrogen, we have
\[ U(K) = -2(12\pi^2)^{-1/3} r_s^{-1} u^{-2} \]  
(14)

with
\[ u = K/2k_F, \]  
(15)

and one may easily see that when \( p=0 \) Eq. (11) reduces to the result of Bellemans and De Leener.\(^1\) When \( p\neq 0 \) from Eqs. (2) and (13), it follows that
\[ u \pm = u \{1 \pm (1/3)p + (2/9)p^2 + \cdots \}. \]  
(16)

Substituting Eq. (16) in Eq. (11), retaining terms up to the order of \( p^2 \) and combining the result with Eq. (3), we get
\[ \alpha_L = -\frac{2r_s^2}{9(12\pi^2)^{1/3}K^{2/3}} \left\{ \frac{|U(K)|^2}{u^2 - 1} \left[ 1 + \frac{1-u^2}{2u} \ln \left| \frac{1+u}{1-u} \right| \right] \right\}. \]  
(17)

For metallic hydrogen, substituting Eq. (14) in Eq. (17) and performing a relevant lattice sum, we have \( \alpha_L \approx -0.117 \) for the bcc arrangement of positive charges.

§ 3. Application to alkali metals

The paramagnetic susceptibility \( \chi \) per unit volume is expressed as
\[ \chi = \chi_0 (\alpha_F/\alpha), \]  
(18)

where \( \chi_0 \) is the susceptibility of free electrons:
\[ \chi_0 = 3fJ^2n/2E_F, \]  
(19)

where \( fJ \) is the electron magnetic moment and \( E_F \) the Fermi energy.

In view of the approximations involved in our theory where the deviation from the free electron model is assumed to be small, our results would be expected to apply to alkali metals. In an actual application, however, one has to take the effect of core electrons into account, and this will be done as follows.

Let a potential between an electron and a lattice point be \( u(\mathbf{x}) \). Then the lattice potential \( U(\mathbf{r}) \) is written as
\[ U(\mathbf{r}) = \sum_\alpha u(\mathbf{r} - \mathbf{x}_\alpha), \]  
(20)

where the summation is extended over all the lattice points. If we define a Fourier transform:
\[ u(\mathbf{k}) = \int u(\mathbf{x}) \exp(-i\mathbf{k} \cdot \mathbf{x}) \, d\mathbf{x}, \]  
(21)

it is easily proved that
where \( n_t \) is the number density of positive charges.

It has recently\(^6\) been pointed out that even though there is a very strong negative potential energy well for an electron near atomic nucleus, it is approximately cancelled out by high kinetic energy associated with the rapid oscillations of the wave function within the region of the ion core. Then one is left with a weak pseudopotential which may be treated by perturbation method. One of the simplest ways of defining the pseudopotential is to use a modified Coulomb potential as Bellemans and De Leener\(^7\) have done. Suppose that \( u(x) \) is given by

\[
    u(x) = \begin{cases} 
    -\frac{2}{r}, & |x| > r_0 \\
    0, & r < r_0
    \end{cases}
\]

Then by the use of Eq. (22), we have

\[
    U(K) = -\frac{2\pi n_t}{K^3} \cos Kr_0.
\]

In Eqs. (23) and (24), \( r_0 \) is a cutoff parameter which is related to the specific nature of the metal under consideration. Here we assume rather arbitrarily \( r_0 = 1.0, 1.5 \) and \( 2.0 \), and carry out the calculation of \( \alpha_L \) by using Eqs. (17) and (24). The results for bcc Li and Na are shown in Table I.

In Table I \( z \) is measured in units of \( 10^{-6} \) cgs volume unit. (We shall use the same unit in the following.) On the other hand, the experimental results are \( 2.08 \pm 0.1 \) for Li\(^6\) and \( 1.09 \pm 0.08 \) for Na.\(^5\) One may see that the result for Na is rather in good agreement with experiment, but for Li this is not the case. This suggests that the modified Coulomb potential given by Eq. (23) is not suitable for Li. In order to clarify this point we proceed as follows.

Table Ia. Results for Li (\( r_g = 3.22 \)).

<table>
<thead>
<tr>
<th>( r_0 )</th>
<th>( \alpha_L )</th>
<th>( \alpha )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-0.006</td>
<td>0.360</td>
<td>1.05</td>
</tr>
<tr>
<td>1.5</td>
<td>-0.026</td>
<td>0.340</td>
<td>1.12</td>
</tr>
<tr>
<td>2.0</td>
<td>-0.099</td>
<td>0.267</td>
<td>1.42</td>
</tr>
</tbody>
</table>

Table Ib. Results for Na (\( r_g = 3.96 \)).

<table>
<thead>
<tr>
<th>( r_0 )</th>
<th>( \alpha_L )</th>
<th>( \alpha )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-0.023</td>
<td>0.216</td>
<td>0.94</td>
</tr>
<tr>
<td>1.5</td>
<td>-0.001</td>
<td>0.238</td>
<td>0.86</td>
</tr>
<tr>
<td>2.0</td>
<td>-0.042</td>
<td>0.197</td>
<td>1.03</td>
</tr>
</tbody>
</table>

An extensive study of band structure and Fermi surface for alkali metals has been done quite recently by various authors\(^6,7\). If one assumes that the nearly-free electron approximation is valid in this case, the \( U(K) \) is determined by the energy gap at the boundary of Brillouin zone. The value of \( U(K) \) thus determined is shown\(^8\) in Table II for the smallest value of \( K (=2\sqrt{2}\pi/a, a: \text{ lattice constant}) \).

If one uses Eq. (24), the maximum value of \( U(K) \) at \( K = 2\sqrt{2}\pi/a \) is calculated to be \( 0.313 \, r_s^{-1} \). For Li this takes the value 0.097, so that one
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cannot adjust the parameter $r_0$ to the result of band calculation.

Since the dominant contribution to $\alpha_L$ comes from reciprocal lattice points with the smallest $K$, one may evaluate $\alpha_L$ by using $U(K)$ in Table II. The numerical values of $\alpha_L$ thus calculated are tabulated in Table III, together with the relevant quantities. In this table, $\alpha_L$ in parentheses is calculated on the basis of the Bohm-Pines theory:

$$
\alpha_L = 0.162 - 0.0432 r_s^{-1/2} - 0.0032 r_s,
$$

and $\alpha_{B-P}$ is the value derived from the same theory.

<table>
<thead>
<tr>
<th></th>
<th>$r_s$</th>
<th>$U(K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>3.22</td>
<td>+0.1124</td>
</tr>
<tr>
<td>Na</td>
<td>3.96</td>
<td>+0.0096</td>
</tr>
<tr>
<td>K</td>
<td>4.87</td>
<td>-0.0184</td>
</tr>
<tr>
<td>Rb</td>
<td>5.18</td>
<td>-0.0324</td>
</tr>
<tr>
<td>Cs</td>
<td>5.57</td>
<td>-0.0478</td>
</tr>
</tbody>
</table>

As is seen from Table III, for Li and Na the value of $z$ of our theory is fairly close to $\alpha_{B-P}$ and to experimental one. However, a large discrepancy with $\alpha_{B-P}$ is observed for Cs. This may be due to the fact that Cs has the largest $r_s$, so that our theory, which is valid only at a high density limit, cannot be applied to this case. At present, however, there are no available experimental data for Cs, and therefore a decisive conclusion cannot be drawn.

§ 4. Discussions

A systematic approach to the many-body problem of electron gas based on the partial summation of perturbation series yields the results which are valid only at a high density limit. There is little hope of expecting that these high density results are applicable to actual metals. However, if one takes account

Table II. The value of $U(K)$ at $K=2\sqrt{2} \pi/a$

Table III. $\alpha$ for alkali metals. $\alpha_{B-P}$ is due to the Bohm-Pines theory, $\alpha_{ex}$ is the experimental value.

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_p$</td>
<td>0.474</td>
<td>0.313</td>
<td>0.207</td>
<td>0.183</td>
<td>0.158</td>
</tr>
<tr>
<td>$\alpha_{ex}$</td>
<td>-0.253</td>
<td>-0.206</td>
<td>-0.167</td>
<td>-0.157</td>
<td>-0.146</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.145</td>
<td>0.132</td>
<td>0.118</td>
<td>0.114</td>
<td>0.109</td>
</tr>
<tr>
<td>$\alpha_L$</td>
<td>(0.123)</td>
<td>(0.127)</td>
<td>(0.126)</td>
<td>(0.126)</td>
<td>(0.126)</td>
</tr>
<tr>
<td>$z_0$</td>
<td>0.802</td>
<td>0.652</td>
<td>0.529</td>
<td>0.498</td>
<td>0.463</td>
</tr>
<tr>
<td>$z$</td>
<td>1.79</td>
<td>0.86</td>
<td>0.73</td>
<td>0.85</td>
<td>1.78</td>
</tr>
<tr>
<td>$z_{B-P}$</td>
<td>1.90</td>
<td>0.85</td>
<td>0.60</td>
<td>0.52</td>
<td>0.43</td>
</tr>
<tr>
<td>$\alpha_{ex}$</td>
<td>2.08</td>
<td>1.09</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

by guest on 15 September 2017
explicitly of the lattice of positive charges, one may hope the range of validity of approximation becomes much more improved, because electrons have a tendency of localizing around positive charges and the electron density becomes effectively large as compared to the case where the positive charges are smeared out. This situation may be seen mathematically as follows.

Let \( \varepsilon(x) \) be the energy per electron at the ground state. If one puts \( g(\lambda) = \lambda^2 \varepsilon(x) \), \( g(\lambda) \) should satisfy a relation \( g''(\lambda) \leq 0 \), as Ferrell\(^{10}\) has proved. His proof is easily extended to the case of metallic hydrogen, and one may obtain the same inequality.

Now the above-mentioned relation yields\(^{10}\) \( \lambda \leq 1.05 \) for the electron gas in the uniform positive charge background. If we assume that positive charges form the bcc crystal structure, we have

\[
\varepsilon(\lambda) = 2.21 \lambda^{-2} - 2.71 \lambda^{-1} + 0.0622 \ln \lambda - 0.198,
\]

whence it follows \( \lambda \leq 5.37 \). Therefore, one may expect that the results for the electron gas are improved if one takes the lattice of positive charges into consideration without smearing them.

In this paper we did not consider the effect of electron-phonon interaction. As for this problem, Quinn\(^{11}\) has pointed out that at the lowest order approximation it gives no contribution to spin paramagnetism, irrespectively of the exact form of matrix element giving rise to the scattering of electron by phonon, and whether the Umklapp processes are included or not. However, this interaction gives a dominant contribution to specific heat, and we shall discuss this problem in another occasion.

In conclusion the author would like to express his sincere thanks to Professor S. Nakajima and Mr. M. Watabe for their valuable discussions.

References

9) J. M. Ziman, Phil. Mag. 6 (1961), 1013.