Continuity between Bound and Unbound States in a Fermi Gas*

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A soluble model of a gas of independent fermions in the presence of an attractive localized potential $\lambda v(\mathbf{r})$ is considered. It is shown that the properties of the system as a whole are smooth (analytic) functions of λ, even at those values of λ where new single-particle bound states appear. Thus for the system as a whole, the transition from "screening" to "binding" is smooth and the concept of a bound state cannot be given a sharp meaning. Implications for certain metals and alloys are discussed.

1. INTRODUCTION

WHEN a single particle moves in an external, short-range potential $\lambda v(\mathbf{r})$, there is a sharp distinction between bound states and unbound states. In infinite space the former are quadratically integrable, the latter are not. If, as is customary, the system is enclosed in a large box of volume Ω and if $v(\mathbf{r})$ is taken as localized near the origin, then the normalized eigenfunctions have the properties

$$\lim_{\Omega\to\infty}|\psi(0)|^2=\begin{cases}p>0 & \text{bound state},\\ =0 & \text{unbound state}.\end{cases} \tag{1.1}$$

Thus there are quite sharp criteria to distinguish between these two types of states.

Let us next consider a particular state as a function of λ, first for finite but large Ω. The energy $E_\Omega(\lambda)$ will have the qualitative behavior shown in Fig. 1(a). As $\Omega\to\infty$, then $E_\Omega(\lambda)\to E_\infty(\lambda)$, shown in Fig. 1(b). This is nonanalytic at $\lambda=\lambda_1$, which separates the bound from the unbound ranges. These are all familiar facts.

In the present note, we consider the properties of a degenerate Fermi *gas*, when placed in an enclosure with an attractive potential $\lambda v(\mathbf{r})$ in its center. Now in analogy with what has just been said, one might expect that when λ exceeds certain critical values $\lambda_1, \lambda_2, \cdots$ the potential will bind 1, 2, $\cdots$ particles and that at these values of λ some properties of the system will change in a nonanalytic fashion. We shall, however, show in a simple, soluble example that this is not the case. The example is a gas of noninteracting particles in a spherical box containing a spherically symmetric potential at its center. We shall see that even though individual states behave nonanalytically at $\lambda_1, \lambda_2, \cdots$ the properties of the *entire* system are analytic there, even in the limit where $\Omega\to\infty$, while the density is kept constant. Thus for the system as a whole, the transition from very small λ (screening) to large λ (binding) is completely smooth. This means that the very notion of "bound state" in such a system is not meaningful.

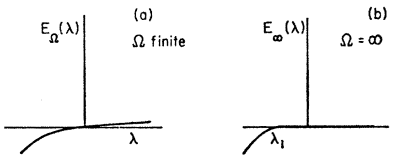

FIG. 1. Transition between bound and unbound states for a single particle.

2. ANALYTIC PROPERTIES OF THE DENSITY MATRIX

Because of the spherical symmetry of our system, we can separate in spherical coordinates which leads to a series of one-dimensional problems. We shall from here on deal only with $l=0$, which is governed by the differential equation

$$H\psi\equiv[-(d^2/dx^2)+\lambda v(x)]\psi=E\psi. \tag{2.1}$$

For simplicity we assume $v(x)=0$ for $x>a$ and, throughout, we shall restrict λ by the requirement

$$|\lambda|\leqslant\Lambda, \tag{2.2}$$

where Λ is a fixed but arbitrarily large number.[1] We write the radius of our enclosure $R=L+a$ (see Fig. 2), so that the eigenfunctions $\psi_n(x,\lambda)$ of H satisfy the boundary conditions

$$\psi_n(0,\lambda)=\psi_n(L+a,\lambda)=0. \tag{2.3}$$

Suppose we are dealing with N particles.[2] Then the physical equilibrium properties of the system as a whole are determined by the density matrix,

$$\rho(x,x';\lambda)=\sum_1^N\psi_n(x,\lambda)\psi_n(x',\lambda), \tag{2.4}$$

where the ψ_n are the real normalized eigenfunctions. For

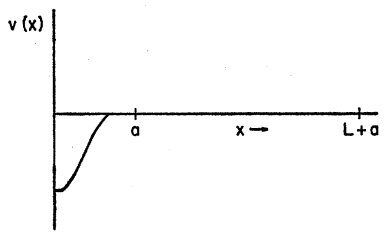

FIG. 2. The potential $v(x)$ and the intervals.

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[1] This avoids certain irrelevant problems of uniform convergence.

[2] We ignore the spin degree of freedom, which is of no interest in this model.

example, the density is given by

$$n(x,\lambda)=\rho(x,x;\lambda), \tag{2.5}$$

and the total energy is

$$\mathcal{E}(\lambda)=\frac{1}{2}\int\left[\frac{\partial}{\partial x}\frac{\partial}{\partial x'}\rho(x,x';\lambda)\right]_{x=x'}dx + \lambda\int v(x)\rho(x,x;\lambda)dx. \tag{2.6}$$

(*Note added in proof.* In this model of noninteracting electrons certain response functions, e.g., that corresponding to optical excitation by light of finite frequency, show nonanalyticities at $\lambda=\lambda_1, \lambda_2, \cdots$. However, even those nonanalyticities disappear as soon as interactions are included because they lead to an Auger broadening of excited levels of the system. Thus our conclusion that there is no sharp transition between "bound" and "unbound" states remains valid.)

We wish to establish the analyticity of ρ as function of λ in a strip enclosing the real λ axis, which remains of finite width even when $L\to\infty$. This will imply the required result that, for real λ, ρ remains a "smooth" function of λ up to the arbitrarily large limits $\pm\Lambda$.

We must then define an analytic continuation of $\rho(x,x';\lambda)$ into the complex λ plane. For this purpose we introduce the function $\psi(x;E,\lambda)$ which, for all complex λ and E, satisfies the differential equation (2.1) and the initial conditions

$$\psi(0;E,\lambda)=0, \quad \psi'(0;E,\lambda)=1. \tag{2.7}$$

It is known[3] that this is an entire function of both E and λ. Next we define the complex eigenvalues $E_n(\lambda)$ as those values of E for which also the second boundary condition (2.3) is satisfied, i.e.,

$$\psi(L+a;E_n(\lambda),\lambda)=0. \tag{2.8}$$

The complex normalization is defined by

$$N(E,\lambda)\equiv\int_0^{L+a}[\psi(x;E,\lambda)]^2dx. \tag{2.9}$$

With these definitions, the analytic continuation of ρ into the complex λ plane is given by

$$\rho(x,x';\lambda)=\sum_{n=1}^{N}\frac{\psi(x;E_n(\lambda),\lambda)\psi(x';E_n(\lambda),\lambda)}{N(E_n(\lambda),\lambda)}. \tag{2.10}$$

Figure 3 shows a schematic representation of the eigenvalues $E_n(\lambda)$ for real λ. When λ acquires an imaginary part, the eigenvalues move into the complex plane. A singularity of ρ as function of λ could then arise either as a result of a singularity of one or more of the $E_n(\lambda)$, or from a zero of $N(E_n(\lambda),\lambda)$, or a combination of both.

[3] H. Poincaré, Acta Math. 4, 215 (1884).

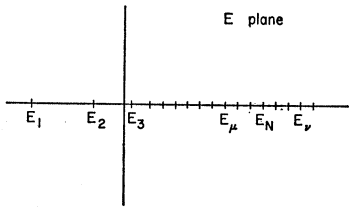

FIG. 3. Eigenvalues for real λ.

Let us begin by examining the singularities of $E_n(\lambda)$. These eigenvalues are, by definition, roots of the equation

$$\psi(L+a;E,\lambda)=0, \tag{2.11}$$

from which we find

$$\frac{dE}{d\lambda}=-\frac{\partial\psi(L+a;E,\lambda)}{\partial\lambda}\Big/\frac{\partial\psi(L+a;E,\lambda)}{\partial E}. \tag{2.12}$$

Thus $E(\lambda)$ can be singular only where also

$$\frac{\partial\psi(L+a;E,\lambda)}{\partial E}=0. \tag{2.13}$$

At such a point it has in general a branch point of the square-root type.[4] If we denote such a point by (λ_s,E_s), then we have, in its vicinity,

$$(E-E_s)^2=c(\lambda-\lambda_s)+\cdots. \tag{2.14}$$

Next we note that Eqs. (2.1) and (2.9) yield immediately

$$N(E_n(\lambda),\lambda)=\int_0^a v(x)[\psi(x;E_n(\lambda),\lambda)]^2dx\Big/\frac{dE_n(\lambda)}{d\lambda}, \tag{2.15}$$

so that in view of (2.13),[5]

$$N(E_s,\lambda_s)=0. \tag{2.16}$$

Thus, near this point we may, in general, write

$$N(E,\lambda)=A_1(E-E_s)+B_1(\lambda-\lambda_s)+\cdots. \tag{2.17}$$

Now, for λ near λ_s, let us call the two roots of (2.14) E_μ and E_ν and assume that both μ and ν are $\leqslant N$. Then clearly the *sum* of the two contributions of μ and ν to (2.10) is single-valued as we go around λ_s. Also from (2.14) and (2.17) we find that at $\lambda=\lambda_s$ this sum is finite, because of the cancellation of the singularities.

Thus we draw the following conclusion: Only those branch points of the multivalued function $E(\lambda)$ can give rise to a singularity of $\rho(x,x';\lambda)$ which involve one eigenvalue, E_μ with $\mu\leqslant N$, and another E_ν with $\nu\geqslant N+1$.

[4] Higher roots would require higher energy derivatives also to vanish. In general, the resulting set of equations linking λ and E is then overdetermined. We shall therefore not pursue this possibility further. We shall also ignore the accidental possibility of having $\partial\psi/\partial\lambda=0$ as well.

[5] We exclude the accidental case where the numerator of (2.16) also vanishes at (λ_s,E_s).

Coalescence of two eigenvalues E_μ and E_ν with both μ and $\nu \leqslant N$ does not make ρ singular.

Next we turn to the possibility of singularities of ρ due to those zeros of N which are not associated with a branch point (λ_s, E_s). At such a singularity, (λ, E), the following relations would have to be satisfied:

$$\psi(L+a; E, \lambda)=0, \tag{2.18}$$

$$N \equiv \int_0^{L+a} [\psi(x; E, \lambda)]^2 dx = 0, \tag{2.19}$$

and, since by assumption $dE/d\lambda \neq \infty$, one finds from (2.15) also

$$\int v(x)[\psi(x; E, \lambda)]^2 dx = 0. \tag{2.20}$$

These equations are overdetermined and in general will have no solution. We shall therefore give no further consideration to this conceivable source of singularities.

3. ABSENCE OF BRANCH POINTS IN A FINITE STRIP ENCLOSING THE REAL λ AXIS

In this section we wish to show that two eigenvalues $E_\mu (\mu \leqslant N)$ and $E_\nu (\nu \geqslant N+1)$ cannot coalesce unless $|\mathrm{Im}\lambda|$ exceeds a certain $\lambda_2{}^{\min}$ which remains finite when $L \to \infty$. It is convenient to work in the κ plane, with the notation $\kappa^2 = E$.

The following result is proved in the Appendix: Provided that

$$|\lambda| \leq \Lambda, \quad |\mathrm{Im}\lambda| \leq \lambda_2', \tag{3.1}$$

where λ_2' is a number independent of L; provided that κ lies inside the shaded half-strip S of Fig. 4, and provided that L is sufficiently large; then

$$\left|\frac{d\kappa}{d\lambda}\right| \leqslant \frac{m}{L}, \tag{3.2}$$

where m is a positive number independent of L.[6]

Now suppose that $\kappa_\mu (\mu \leqslant N)$ and $\kappa_\nu (\nu \geqslant N+1)$ coalesce for $\lambda_s = \lambda_{s1} + i\lambda_{s2}$. For *real* λ the roots $\kappa_n (n \gg 1)$ have, with an accuracy of $O(L^{-2})$, the same spacing π/L as for free particles. Hence, for $\lambda = \lambda_{s1}$

$$|\kappa_\nu - \kappa_\mu| > \pi/2L. \tag{3.3}$$

Also, since $\kappa_\nu(\lambda_{s1})$ is inside our strip and hence more than a distance $\pi/4L$ from its boundary, it is evident that as λ changes from λ_{s1} to $\lambda_{s1} + i\lambda_{s2}$, the sum of the distances traced out, inside our strip, by κ_μ and κ_ν must exceed $\pi/4L$ (see Fig. 4). By (3.2), this means that λ_{s2} must have a certain minimum value. In fact, from (3.1), (3.2), and (3.3), it follows that λ_{s2} cannot be less than both λ_2' and $\lambda_2'' = \pi/8m$.

[6] This result is precisely what one would guess from a perturbation estimate.

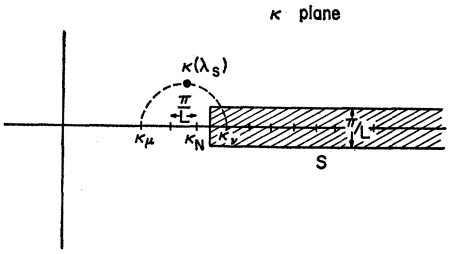

FIG. 4. Coalescing of eigenvalues in the κ plane.

Thus the coalescence cannot occur, and hence ρ cannot have a branch point, as long as

$$|\lambda| \leq \Lambda \quad \text{and} \quad |\mathrm{Im}\lambda| < \lambda_2{}^{\min}, \tag{3.4}$$

where

$$\lambda_2{}^{\min} = \min(\lambda_2', \lambda_2''). \tag{3.5}$$

4. CONCLUDING REMARKS

We have just proved the smoothness of transition between bound and unbound states in a degenerate Fermi gas, for a certain simple model. There is little doubt that this continuity will hold under a much wider set of conditions, e.g., finite temperature, a periodic array of potentials (with certain exceptions), and systems with sufficiently weak interactions. We believe that the conclusions of this paper have relevance to such dilute, nonmagnetic alloys as Zn, Ga, Ge, and As in a Cu matrix.[7] The properties of this sequence of systems appear indeed to be smooth functions of the valence of the solute.

The present paper may also shed some light on recent experimental results[8] showing the possibility of a smooth transition between two phases of metallic Ce, one of which is generally regarded as arising from the other by the release of an f electron from a "bound" state into the conduction band.

However, very strong interactions between electrons may well lead to radically different situations. There exists today strong evidence, both experimental[9] and theoretical[10] for the occurrence, in some cases, of localized magnetic moments associated with impurity atoms. These differ qualitatively from our model because electron-electron interaction is essential for their existence.

ACKNOWLEDGMENTS

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[9] B. T. Matthias, M. Peter, H. J. Williams, A. M. Clogston, E. Corenzwit, and R. C. Sherwood, Phys. Rev. Letters **5**, 542 (1960).
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APPENDIX: DEPENDENCE OF EIGENVALUES ON λ

To locate the branch points λ_s of ρ which correspond to the coalescence of eigenvalues, we must now study in somewhat greater detail the dependence of these eigenvalues on λ. We therefore turn to the eigenvalue problem defined by Eqs. (2.1) and (2.3).

In the interval $0\leqslant x\leqslant a$ we must solve the equation

$$[-(d^2/dx^2)+\lambda v(x)-\kappa^2]\varphi_1(x;\kappa,\lambda)=0, \quad \text{(A1)}$$

where we have written $E=\kappa^2$. To the boundary condition

$$\varphi_1(0;\kappa,\lambda)=0, \quad \text{(A2)}$$

we may add

$$\varphi_1'(0;\kappa,\lambda)=1, \quad \text{(A3)}$$

which has the important consequence that this φ_1 is an entire function of both κ and λ[3]. We denote the logarithmic derivative of φ_1, at $x=a$ by

$$L(\kappa,\lambda)\equiv[(d/dx)\varphi_1(x;\kappa,\lambda)/\varphi_1(x;\kappa,\lambda)]_{x=a}. \quad \text{(A4)}$$

In the interval $a\leqslant x\leqslant L+a$, we solve the free equation

$$(-(d^2/dx^2)+\kappa^2)\varphi_2(x;\kappa,\lambda)=0, \quad \text{(A5)}$$

subject to the boundary condition

$$\varphi_2(L+a;\kappa,\lambda)=0. \quad \text{(A6)}$$

This gives

$$\varphi_2(x;\kappa,\lambda)=A\sin[\kappa(x-L-a)]. \quad \text{(A7)}$$

The dependence of κ on λ is obtained by equating the logarithmic derivatives of φ_1 and φ_2 at $x=a$. This gives

$$-\kappa\cot\kappa L=L(\kappa,\lambda). \quad \text{(A8)}$$

For a given λ, the roots of this equation are the required eigenvalues. Equivalently we may define the phase shift

$$\eta(\kappa,\lambda)\equiv\cot^{-1}[-L(\kappa,\lambda)/\kappa]+\kappa a, \quad \text{(A9)}$$

and replace (A8) by

$$\eta(\kappa,\lambda)=\kappa(L+a)+n\pi, \quad n=0,\pm1,\cdots. \quad \text{(A10)}$$

This expresses the fact that κ and λ are multivalued functions of each other. Since φ_1 is an entire function of λ and κ, it follows by (A4) that $[L(\kappa,\lambda)/\kappa]$ is a meromorphic function of these variables. Hence, by (A9), η is an analytic function of κ and λ except where

$$L(\kappa,\lambda)/\kappa=\pm i. \quad \text{(A11)}$$

We shall wish to establish the upper bound (3.2) on $|d\kappa/d\lambda|$. By (A10) the required quantity is given by

$$\frac{d\kappa}{d\lambda}=\frac{\partial\eta/\partial\lambda}{(L+a)-\partial\eta/\partial\kappa}. \quad \text{(A12)}$$

Therefore, we need to show that, under the conditions stated in Sec. 3, $|\partial\eta/\partial\lambda|$ and $|\partial\eta/\partial\kappa|$ have finite bounds, independent of L.

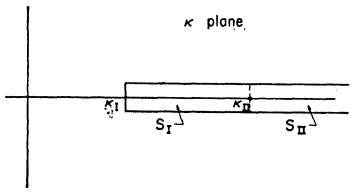

FIG. 5. The two regions $S_{\rm I}$, $S_{\rm II}$.

To progress further we divide the inside of the half-strip S of Fig. 4 into two regions, $S_{\rm I}$ and $S_{\rm II}$, as shown in Fig. 5, where $\kappa_{\rm II}$ is a large value to be chosen presently.

Region $S_{\rm II}$

Since λ is limited by $|\lambda|\leqslant\Lambda$, we can choose $\kappa_{\rm II}$ so large that for all λ under consideration η can be estimated by Born approximation

$$\eta\sim-\frac{\lambda}{\kappa}\int_0^a v(x)\sin^2\kappa x dx, \quad \text{(A13)}$$

which gives, by (A12), for large enough L

$$\frac{d\kappa}{d\lambda}\sim\frac{1}{L}\frac{1}{\kappa}\int_0^a v(x)\sin^2\kappa x dx. \quad \text{(A14)}$$

Hence we can find a sufficiently large $\kappa_{\rm II}$ such that in $S_{\rm II}$

$$|d\kappa/d\lambda|<m'/L, \quad \text{(A15)}$$

where[11]

$$m'=\frac{1}{\kappa_{\rm II}}\int_0^a v(x)dx. \quad \text{(A16)}$$

Region $S_{\rm I}$

Restrict first κ to the real axis. Then η is regular for real λ, by (A11), since $L(\kappa,\lambda)$ is real for real κ and λ. Let $\lambda=l_1+il_2$ be that solution of (A11) which has the smallest $|l_2|$.

Now if κ is allowed to become complex, but confined to the narrow region $S_{\rm I}$, of width π/L, it is clear that, for L large enough, all solutions λ of (A11) will have $|{\rm Im}\lambda|>|l_2|/2$. Hence if we consider only such λ for which $|{\rm Im}\lambda|<|l_2|/4$, then $|\partial\eta/\partial\lambda|$ and $|\partial\eta/\partial\kappa|$ have finite bounds, say b_1 and b_2. Hence, for L large enough we have in $S_{\rm I}$,

$$|d\kappa/d\lambda|<m''/L, \quad m''=2b_1, \quad \text{(A17)}$$

provided that

$$|{\rm Im}\lambda|\leqslant\lambda_2', \quad \text{(A18)}$$

where $\lambda_2'=|l_2|/4$.

Combining (A15) and (A17) gives the required result,

$$|d\kappa/d\lambda|<m/L, \quad m=\min(m',m''), \quad \text{(A19)}$$

under the conditions given in Sec. 3.

[11] This expression diverges if $v(x)\sim1/x$ for small x. But also in this case one can easily establish a result of the form (A15).