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Quantum Density Oscillations in an Inhomogeneous Electron Gas*

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An infinite system of electrons in its ground state, subject to a very slowly varying external potential, has slowly varying properties, and can be described by a gradient expansion theory. However, when, in addition, either (1) there is a spatially rapidly varying perturbing potential, or (2) there are regions in which the electron density drops to zero (e.g., electrons in an oscillator potential), the density and other properties of the system exhibit additional spatial oscillations, which we call quantum oscillations. An example are the Friedel oscillations in metals. In the present paper we develop a general theory of these oscillations for one-dimensional, noninteracting electrons. Illustrations are worked out which show that when the quantum oscillations are superposed on the smooth "semiclassical" results, one can obtain very accurate approximations to the exact densities.

I. INTRODUCTION

THIS paper deals with some general features of systems of electrons in their ground state.

Our starting point is an infinite electron gas, subject to a sufficiently slowly varying external potential, $v(\mathbf{r})$. Such a situation is adequately governed by a theory in which the energy is expressed as a functional $E[n(\mathbf{r})]$ of the density $n(\mathbf{r})$, and this functional is expanded in a series involving derivatives of the density.[1] From such a theory one derives a density distribution $n(\mathbf{r})$ whose spatial variation parallels that of the external potential. Thus, the smoother this potential, the smoother the corresponding density. The same is true for all other position-dependent properties of the gas. This type of approach may be regarded as a systematic extension of the semiclassical Thomas-Fermi method.

However, the gradient expansion for $E[n]$ breaks down when: (1) in addition to a smooth potential, $v^s(\mathbf{r})$, there is present a spatially rapidly varying potential $v'(\mathbf{r})$; or (2) there are regions in which the electron density drops to zero, as is for example the case for an atom at large distances from the nucleus. In such cases, the electronic density $n(\mathbf{r})$, as well as other properties, exhibits additional spatial oscillations which are no longer determined solely by the behavior of the potential in the neighborhood of $\mathbf{r}$. Such oscillations, which are not obtainable from the semiclassical[2] gradient expansion for $E[n]$, taken to any finite order, we call quantum density oscillations. A well-known example is the Friedel oscillations[3] set up by an impurity potential in an otherwise homogeneous electron gas. These oscillations have a wave number of about $2k_F$ (k_F=Fermi momentum) and extend into the region of constant potential.

We are hopeful that when the quantum oscillations are superposed on the results of a semiclassical calculation, one will obtain a rather accurate theory of the electronic structure of a wide class of physical systems. This approach should be especially useful in situations which bear little resemblance to the homogeneous electron gas, and which are therefore not easily amenable to those conventional many-body theories in which translational invariance and, relatedly, the momentum operator play a central role. Examples are atoms, whose shell structure appears in the present context as a manifestation of quantum oscillations, and metallic alloys.

In the present paper we limit ourselves to a study of a one-dimensional, noninteracting electron gas, which already exhibits all the key features to which we have drawn attention. As is usual, we have available for these one dimensional systems special methods which facilitate the calculations. The harmonic oscillator and Coulomb potentials are worked out as examples, and agreement with the exact solutions is very close. We plan in the near future to extend this work to three dimensions and to interacting electrons.

1. Generalities

All physical properties of a system of non-interacting electrons are derivable from the one-particle Green's function $G(x,x';E)$, which satisfies the differential equation

$$\{-(d^2/dx^2)+v(x)-E\}G(x,x')=-\delta(x-x'), \quad (1.1)$$

and the appropriate boundary conditions.

We shall assume that the single-particle energy levels are discrete (if necessary, we confine the electrons to a large box of length $2L$), and denote the normalized, real eigenfunctions by $\psi(x,E_n)$, in terms of which the Green's function can be written as

$$G(x,x';E)=\sum_m\psi(x,E_m)\psi(x',E_m)/(E-E_m). \quad (1.2)$$

In one dimension another useful form for the Green's function exists. Let ψ_1 and ψ_2 be two solutions of the

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[1] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964). See in particular Eqs. (15), (64), and (63). Exchange and correlation effects can be included in each order of this gradient expansion.

[2] In this paper "semiclassical" denotes a situation with a sufficiently slowly varying potential, which may be described by a gradient expansion (cf. Ref. 1, Part III). The Pauli principle and, in the case of interacting systems, exchange and correlation effects are meant to be included.

[3] J. Friedel, Phil. Mag. 43, 153 (1952).

Schrödinger equation

$$\{-(d^2/dx^2)+v(x)-E\}\psi(x,E)=0\,, \qquad (1.3)$$

which satisfy the boundary condition on the left and on the right, respectively, and denote the Wronskian by

$$W(E)\equiv\psi_1(x,E)[\partial\psi_2(x,E)/\partial x] \\ -\psi_2(x,E)[\partial\psi_1(x,E)/\partial x]. \qquad (1.4)$$

Then

$$G(x,x';E)=[\psi_1(x,E)\psi_2(x',E)]/W(E)]\,,\ \text{for } x\leqslant x'\,, \quad (1.5) \\ =[\psi_2(x,E)\psi_1(x',E)/W(E)]\,,\ \text{for } x\geqslant x'.$$

We shall make extensive use of this form.

An example of the use of the Green's function is the following expression for the particle density $n(x)$,

$$n(x)=(1/2\pi i)\oint_C dE\, G(x;E)\,, \qquad (1.6)$$

where we use the abbreviated notation

$$G(x;E)\equiv G(x,x;E). \qquad (1.7)$$

C is a contour in the complex E plane which encloses the lowest N eigenvalues, E_m, where N is the number of electrons[4] (see Fig. 1). The correctness of (1.6) follows immediately from the form (1.2) for G.

In the particular case of electrons moving in a constant potential v_0 and confined to a box $-L\leqslant x\leqslant L$, the form (1.5) leads to the following explicit expression:

$$G_0(x,x';E)=\frac{\sin\{(E-v_0)^{1/2}(x+L)\}\,\sin\{(E-v_0)^{1/2}(x'-L)\}}{(E-v_0)^{1/2}\sin\{2(E-v_0)^{1/2}L\}}\,,\quad x\leq x'\,, \\ =\frac{\sin\{(E-v_0)^{1/2}(x-L)\}\,\sin\{(E-v_0)^{1/2}(x'+L)\}}{(E-v_0)^{1/2}\sin\{2(E-v_0)^{1/2}L\}}\,,\quad x\geq x'. \qquad (1.8)$$

Here we choose for $(E-v_0)^{1/2}$ the branch which is positive for $(E-v_0)$ just above the positive real axis. In spite of the appearance of the square roots, the Green's function has no branch points, for finite L. For $L\to\infty$, its poles become dense and form a branch line extending along the real axis from v_0 to $+\infty$. In that limit

$$G_0(x,x';E)=[1/2i(E-v_0)^{1/2}]e^{i(E-v_0)^{1/2}|x-x'|}. \qquad (1.9)$$

Let us now consider the behavior of G for large values of E, in the case of a general potential $v(x)$. We relate this to the free case just considered by means of the integral equation[5]

$$G(x,x')=G_0(x,x')+\int_{-L}^{L}dx'' \\ \times G_0(x,x'')\{v(x'')-v_0\}G(x'',x')\,, \qquad (1.10)$$

which may be seen to satisfy (1.1) and boundary conditions. This equation may be solved by iteration leading to a series which converges rapidly for sufficiently large values of E, except near the positive real axis. In this asymptotic region the behavior of G is adequately determined by the first iterate of (1.10). For $x=x'$, one finds after integrations by parts

$$G(x;E)=G_0(x;E)-\frac{i\{v(x)-v_0\}}{4E^{3/2}}-\frac{1}{16E^2}\frac{dv}{dx} \\ +O(|E|^{-5/2}). \qquad (1.11)$$

Note that for such E, $G(x;E)$ is determined by the *local* behavior of the potential. In fact, if for a given x we choose the v_0 in G_0 as equal to $v(x)$, then

$$G(x;E)=G_0(x;E)+O(|E|^{-2}). \qquad (1.12)$$

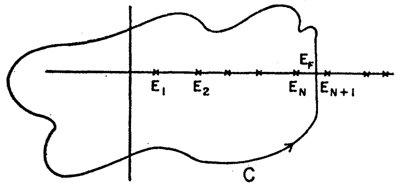

FIG. 1. The contour C used in the integral (1.6).

2. The Semiclassical Solution

In this section we construct the Green's function for the case of a very slowly varying potential, which we denote by $v^s(x)$. We shall require the corresponding G^s on the contour C shown in Fig. 1. We shall call the point between E_N and E_{N+1} where C crosses the real axis the Fermi energy, E_F. In this section we shall assume that for all x, $E_F>v^s(x)$ (see Fig. 2).

It is convenient to use the form (1.5) for G^s in which we take the WKB solutions for ψ_1 and ψ_2

$$\psi_i^s=[2/(p(x,E))^{1/2}]\sin\theta_i(x,E)\,,\quad i=1,2 \qquad (1.13)$$

where

$$p(x,E)=(E-v^s(x))^{1/2}, \qquad (1.14)$$

and

$$\theta_1\equiv\int_{-L}^{x}(E-v^s(t))^{1/2}dt, \\ \theta_2\equiv\int_{x}^{L}(E-v^s(t))^{1/2}dt. \qquad (1.15)$$

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[4] We ignore the spin degree of freedom of the electrons.

[5] For simplicity of writing, the dependence on E, in this and some of the following equations, is not explicitly shown.

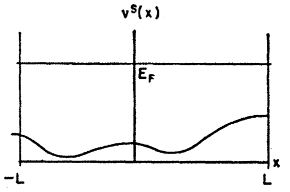

FIG. 2. The semiclassical case.

The convention concerning the square roots is the same as that following Eq. (1.8).

In the limit when $L \to \infty$, for complex E, only one of the two exponentials of $\sin\theta_i$ remains, leading to the result[6]

$$G^s(x,x';E)=[1/2i(p(x,E)p(x',E))^{1/2}]e^{\pm i\theta(x,x';E)}\,, \qquad \text{for } x\lesseqgtr x'\,, \tag{1.16}$$

where

$$\theta(x,x';E)=\int_x^{x'}(E-v^s(t))^{1/2}dt. \tag{1.17}$$

In fact (1.16) is valid except on a branch-cut extending from the minimum value of $v^s(t)$ in the interval (x,x') to $+\infty$.

As a simple application of (1.16) we can obtain the density $n^s(x)$ by substitution into (1.6). The contour integral is elementary and gives

$$n^s(x)=(1/\pi)p(x,E_F)=1/\pi[E_F-v^s(x)]^{1/2}. \tag{1.18}$$

This is just the density of a free one-dimensional electron gas, with maximum energy $E_F-v^s(x)$, i.e., the Thomas-Fermi result for our model.

II. PERTURBING POTENTIALS

1. Polarizability of a Semiclassical Electron Gas

A quantity of considerable interest is the first order change of density, at a point x', in a semiclassical electron[2] gas, due to a perturbing potential at the point x. Accordingly we define the polarizability $\alpha(x,x')$ by the equation

$$n(x)-n^s(x)=\int dx'\,\alpha(x,x')v'(x')\,, \tag{2.1}$$

where v' is a small perturbing potential superposed on the slowly varying potential v^s. Using an integral equation analogous to Eq. (1.10), we have to first order in v'

$$G(x,x')=G^s(x,x') + \int dx''\,G^s(x,x'')v'(x'')G^s(x'',x')\,, \tag{2.2}$$

and hence, by (1.6),

$$\alpha(x,x')=(1/2\pi i)\oint_C dE\,G^s(x,x';E)G^s(x',x;E)\,. \tag{2.3}$$

Here it is convenient to use the contour C of Fig. 3.

For $x\neq x'$ the large circle gives a vanishing contribution and, using the form (1.16) for G^s, we obtain

$$\alpha(x,x')=-\frac{1}{4\pi}\int_{E_F}^{\infty}dE\frac{\sin\{2\theta(x,x';E)\}}{p(x,E)p(x',E)}\,. \tag{2.4}$$

In view of the slow variation of v^s, the integration over E can be carried out as follows. We introduce θ as the new integration variable and write

$$\alpha(x,x')=-\frac{1}{4\pi}\int_{\theta_F}^{\infty}d\theta\left[\frac{2\theta}{p(x,E(\theta))p(x',E(\theta))\tau(x,x';E(\theta))}\right] \times\frac{\sin 2\theta}{\theta}\,, \tag{2.5}$$

where

$$\theta_F\equiv\theta(x,x';E_F)\,, \tag{2.6}$$

and

$$\tau(x,x';E)=\int_x^{x'}\frac{dt}{(E-v^s(t))^{1/2}}\,. \tag{2.7}$$

(τ is the classical time for motion with energy E from x to x'.) For slowly varying v^s, we can replace θ by θ_F in the bracketed factor of (2.5), giving

$$\alpha(x,x')=\frac{\theta(x,x';E_F)}{2\pi p(x,E_F)p(x',E_F)\tau(x,x';E_F)} \times\left\{\mathrm{Si}(2\theta(x,x';E_F))-\frac{\pi}{2}\right\}\,, \tag{2.8}$$

where

$$\mathrm{Si}(\gamma)=\int_0^{\gamma}\frac{\sin\gamma'}{\gamma'}d\gamma'\,. \tag{2.9}$$

The function $\alpha(x,x')$ describes one kind of quantum density oscillations which are the analog of the Friedel oscillations[3] in a background of slowly varying electron density. As may be seen from the asymptotic form of Si (γ),

$$\mathrm{Si}(\gamma)\sim(\pi/2)-(\cos\gamma/\gamma)\,, \tag{2.10}$$

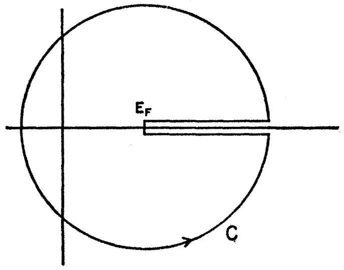

FIG. 3. The contour C used in the integral (2.3).

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[6] The Green's function in a slowly varying potential was first obtained by Baroff and Borowitz [Phys. Rev. **121**, 1704 (1961)], but only for $|x-x'|$ sufficiently small. There is no such restriction in (1.16) and this more general form will be needed in II.2 for developing the theory of quantum density oscillations.

the local wave number of these oscillations equals twice the local Fermi-wave number $(2p(x,E_F))$, but its amplitude and phase depend on the entire functional form of v between x' and x.

In Appendix 1 we work out an example of the density disturbance produced by a δ-function perturbation in a medium of slowly varying density and compare the results with those for a uniform medium.

2. Isolated Disturbance of Arbitrary Magnitude

In the last section, we considered the perturbation produced in a slowly varying medium by a small, but otherwise unrestricted perturbing potential v'. We now discuss the case where v' is localized between two definite limits, a and b, but has arbitrary strength.

We shall be interested in the density changes due to v' outside the interval (a,b), say for $x>b$. For this purpose we require $G(x,x')$, which in analogy to (1.10), could be obtained from the exact solution of the integral equation

$$G(x,x')=G^s(x,x')+\int_a^b dx''\,G^s(x,x'')v(x'')G(x'',x'). \qquad (2.11)$$

Instead it is more convenient to use the form (1.5) of G, and obtain ψ_1 and ψ_2 by matching WKB solutions for the region external to (a,b) with exact solutions inside (a,b).

Inside (a,b) we define two solutions, φ_1 and φ_2, of the Schrödinger equation (1.3), with the total potential $v(x)$, which directly outside of this interval have the following functional form:

$$\begin{aligned}\varphi_1(x)&=[1/(p(a))^{1/2}]\{e^{ip(a)(x-a)}+r_1e^{-ip(a)(x-a)}\}, \quad x=a-0,\\ &=[1/(p(b))^{1/2}]\{t_1e^{ip(b)(x-b)}\}, \quad x=b+0, \qquad (2.12)\end{aligned}$$

and

$$\begin{aligned}\varphi_2(x)&=[1/(p(b))^{1/2}]\{e^{-ip(b)(x-b)}+r_2e^{ip(b)(x-b)}\}, \quad x=b+0,\\ &=[1/(p(a))^{1/2}]\{t_2e^{-ip(a)(x-a)}\}, \quad x=a-0. \qquad (2.13)\end{aligned}$$

The $r_i(E)$ and $t_i(E)$ are reflection and transmission coefficients for waves incident from the left and right. They satisfy the relation

$$t_1=t_2, \qquad (2.14)$$

which follows from the constancy of the Wronskian. In addition, for E real, one also obtains

$$\begin{aligned}|r_1|^2+|t_1|^2&=1,\\ |r_2|^2+|t_2|^2&=1, \qquad (2.15)\\ -r_1t_2^*&=t_1r_2^*.\end{aligned}$$

Suppose we want $G(x,x')$, for $b<x\leqslant x'$. Then by elementary matching procedures one finds

$$\begin{aligned}\psi_1(x)&=-\frac{e^{-i\theta(-L,a)}}{2i(p(x))^{1/2}}\left[\frac{1}{t_2}e^{-i\theta(b,x)}+\frac{r_2}{t_2}e^{i\theta(b,x)}\right],\\ \psi_2(x')&=\frac{e^{i\theta(L,x')}}{2i(p(x'))^{1/2}}, \qquad (2.16)\end{aligned}$$

giving

$$G(x,x')=[1/2i(p(x)p(x'))^{1/2}]\times[e^{-i\theta(b,x)}+r_2e^{i\theta(b,x)}]e^{i\theta(b,x')}. \qquad (2.17)$$

Note that the first term is just G^s of Eq. (1.16).

To obtain the density for $x>b$, we evaluate (1.6) along the contour of Fig. 3. This gives

$$n(x)=n^s(x)+n'(x), \qquad (2.18)$$

where n^s is given in Eq. (1.18) and

$$n'(x)=-\frac{1}{2\pi}\,\mathrm{Re}\int_{E_F}^{+\infty}dE\frac{r_2(E)}{p(x,E)}e^{2i\theta(b,x;E)}; \qquad (2.19)$$

the last integral is evaluated along the upper line of the branch cut. If x is near b, evaluation of (2.19) requires a knowledge of $r_2(E)$ for all real $E>E_F$. However, in the asymptotic region, defined by

$$(x-b)p(x,E_F)\gg 1, \qquad (2.20)$$

the leading contribution of (2.19) can be obtained by an integration by parts, giving

$$n'(x)=\mathrm{Im}\left[\frac{r_2(E_F)}{2\pi p(x,E_F)\tau(b,x;E_F)}e^{2i\theta(b,x;E_F)}\right]. \qquad (2.21)$$

We may note that since $|r_2|\leqslant 1$, the amplitude of asymptotic quantum oscillations set up in a given "medium" by a perturbing potential v' is limited by the upper bound

$$|n'(x)|_{\max}=[2\pi p(x,E_F)\tau(b,x;E_F)]^{-1}, \qquad (2.22)$$

characteristic of the medium, no matter how strong v' is.

III. TURNING POINTS

1. A Single Turning Point

Quantum oscillations are produced not only by rapidly varying perturbing potentials but also by turning points corresponding to the energy E_F, i.e., points where $E_F-v(x)=0$. In this section, we consider such a situation with a smooth potential $v=v^s$ as shown in Fig. 4.

To construct G, by means of Eq. (1.5), we use the general solution of the Schrödinger equation in the

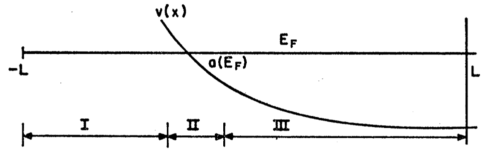

FIG. 4. A slowly varying potential with a single turning point.

presence of a single turning point,[7]

$$\psi(x)=A(8\pi\theta/3p)^{1/2}\{\cos(\tfrac{1}{3}\pi+\eta)J_{1/3}(\theta)+\cos(\tfrac{1}{3}\pi-\eta)J_{-1/3}(\theta)\}\,, \tag{3.1}$$

where

$$\theta\equiv\theta(a(E),x;E)=\int_{a(E)}^{x}(E-v(t))^{1/2}dt; \tag{3.2}$$

the turning point $a(E)$ is defined by

$$v(a(E))=E\,, \tag{3.3}$$

and A and η are arbitrary constants. The Bessel functions J_ν have the following properties[8]:

$$\theta\rightarrow 0:\quad J_\nu(\theta)\sim[1/\Gamma(\nu+1)](\theta/2)^\nu\,,$$
$$\theta\rightarrow\infty:\quad J_\nu(\theta)\sim 1/(2\pi\theta)^{1/2}[c_1e^{i[\theta-\nu(\pi/2)-(\pi/4)]}+c_2e^{-i[\theta-(\nu\pi/2)-(\pi/4)]}]\,, \tag{3.4}$$

where

$$\begin{aligned}&c_1=e^{2l[\nu+(1/2)]\pi i}\,,\\ &c_2=e^{2l[\nu+(1/2)]\pi i}\ (2l-1)\pi<\arg\theta<(2l+1)\pi\,,\\ &c_1=e^{(2l+1)[\nu+(1/2)]\pi i}\,,\\ &c_2=e^{2l[\nu+(1/2)]\pi i}\ 2l\pi<\arg\theta<(2l+2)\pi\,.\end{aligned} \tag{3.5}$$

We shall require the asymptotic forms of $\psi(x)$ for E near E_F, which by (3.5) are

$$\psi(x)\sim(2A/p^{1/2})\cos[\theta+\eta-(\pi/4)]\,,\quad x\rightarrow+\infty\,, \tag{3.6}$$

$$\psi(x)\sim A(e^{i\pi/4}/p^{1/2})(2\sin\eta e^{-i\theta}+\cos\eta e^{-i\theta})\,,\quad x\rightarrow-\infty\,. \tag{3.7}$$

Consequently, for E in the upper half-plane near E_F, wave functions ψ_1 and ψ_2, satisfying the boundary conditions $\psi_1(-L)=0=\psi_2(+L)$, $L\rightarrow\infty$ are

$$\begin{aligned}\psi_1&=(\theta/p)^{1/2}\{J_{1/3}(\theta)+J_{-1/3}(\theta)\}\,,\\ \psi_2&=(\theta/p)^{1/2}\{e^{i\pi/3}J_{1/3}(\theta)+e^{-i\pi/3}J_{-1/3}(\theta)\}\,.\end{aligned} \tag{3.8}$$

By Eq. (1.5) this gives, for $x<x'$,

$$G(x,x')=\frac{\pi}{3i}\left(\frac{\theta(x)\theta(x')}{p(x)p(x')}\right)^{1/2}[J_{1/3}(\theta(x))+J_{-1/3}(\theta(x))]\times[e^{i\pi/3}J_{1/3}(\theta(x'))+e^{-i\pi/3}J_{-1/3}(\theta(x'))]\,. \tag{3.9}$$

By means of this expression we shall now calculate the density $n(x)$. We distinguish three regions (see Fig. 4). Writing $a_F\equiv a(E_F)$ they are

$$\text{Region I:}\quad x<a_F\quad\text{and}\quad|x-a_F|\gg\left|\frac{dv}{dx}\right|_{x=a_F}^{-1/3} \tag{3.10}$$

$$\text{Region II:}\quad |x-a_F|\ll\left|\frac{dv}{dx}\Big/\frac{d^2v}{dx^2}\right|_{x=a_F} \tag{3.11}$$

$$\text{Region III:}\quad x>a_F\quad\text{and}\quad|x-a_F|\gg\left|\frac{dv}{dx}\right|_{x=a_F}^{-1/3}. \tag{3.12}$$

Regions I and III are asymptotic in the sense that, for $E=E_F$, the arguments of the Bessel functions are, in absolute value, much larger than unity; and in region II, $v(x)$ can be adequately expressed as a linear function of x. For a sufficiently slowly varying $v(x)$, region II overlaps regions I and III.

For all three regions we shall evaluate $n(x)$, according to Eq. (1.6), along the contour C of Fig. 5.

Region III: Here $G(x;E)$ reduces to

$$G(x,E)=(1/2ip)-(e^{2i\theta}/2p)\,, \tag{3.13}$$

for E in the upper half plane near E_F.[9] We know from the general discussion of Sec. I [see Eqs. (1.11) and (1.12)] that $G(x;E)$ can differ appreciably from $G^\theta(x,E)=(2ip)^{-1}$ only on a small segment of the straight line portion l, near E_F (see Fig. 5). Accordingly, we have

$$n(x)=n_0(x)+n'(x)\,, \tag{3.14}$$

where

$$n_0(x)=(1/\pi)p(x,E_F)\,, \tag{3.15}$$

and writing $E=E_F+i\zeta$,

$$\begin{aligned}n'(x)&=\mathrm{Re}\frac{1}{\pi}\int_0^\infty d\zeta\left(-\frac{e^{2i\theta}}{2p}\right),\\ &=-\frac{\cos2\theta(a_F,x;E_F)}{2\pi p(x,E_F)\tau(a_F,x;E_F)}\,.\end{aligned} \tag{3.16}$$

These are quantum density oscillations produced by the turning point in the asymptotic region III. Their forms are completely analogous to those produced by a perturbing potential [cf. Eq. (2.21)]. Note that their amplitudes are independent of the details of $v(x)$ near the turning point a_F.

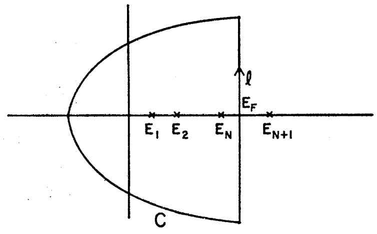

FIG. 5. The semi-circular contour C with radius tending to infinity.

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[7] R. E. Langer, Phys. Rev. **51**, 669 (1937).

[8] G. N. Watson, *A Treatise on the Theory of Bessel Function* (Cambridge University Press, New York, 1922).

[9] Note that $G(x,E)$ has the same form as if in place of the turning point, there were a perturbing potential with reflection coefficient, $r=-i$ [cf. Eq. (2.17)].

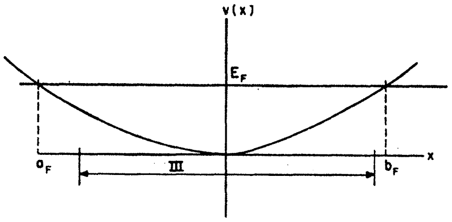

FIG. 6. A slowly varying potential with two turning points.

Region I: Corresponding to (3.13), we have here

$$G(x,E)=(1/4p)(e^{-2i\theta}-2i). \tag{3.17}$$

In this region

$$n_0(x)=0, \tag{3.18}$$

and

$$n'(x)=\frac{\exp\{-2|\theta(a_F,x;E_F)|\}}{4\pi|p(x,E_F)\tau(a_F,x;E_F)|}. \tag{3.19}$$

We see the anticipated exponential decay in the classically forbidden region.

Region II: In this region we write, in view of the linear dependence of v on x,

$$\theta(a(E),x;E)=\left|\frac{3}{2}\frac{dv}{dx}\right|_{x=a_F}^{-1}[E-v(x)]^{3/2}. \tag{3.20}$$

We now change the variable of integration from E to θ. The integrand corresponding to the upper half of l near E_F is given by

$$-\frac{1}{9}\left|\frac{3}{2}\frac{dv}{dx}\right|_{x=a_F}^{1/3}\theta^{1/3}[e^{i\pi/3}J_{1/3}{}^2(\theta)$$
$$+J_{1/3}(\theta)J_{-1/3}(\theta)+e^{-i\pi/3}J_{-1/3}{}^2(\theta)], \tag{3.21}$$

which can be integrated explicitly[8] giving the density as

$$\begin{aligned} n(x)&=\frac{1}{6}\left|\frac{3}{2}\frac{dv}{dx}\right|_{x=a_F}^{1/3}\theta_F{}^{4/3}[\{J_{1/3}(\theta_F)+J_{-1/3}(\theta_F)\}^2 \\ &\quad+\{J_{2/3}(\theta_F)-J_{-2/3}(\theta_F)\}^2],\quad x\geq a_F, \\ &=\frac{1}{6}\left|\frac{3}{2}\frac{dv}{dx}\right|_{x=a_F}^{1/3}|\theta_F|^{4/3}[-\{I_{1/3}(|\theta_F|)-I_{-1/3}(|\theta_F|)\}^2 \\ &\quad+\{I_{2/3}(|\theta_F|)-I_{-2/3}(|\theta_F|)\}^2],\quad x\leq a_F, \end{aligned} \tag{3.22}$$

where θ_F denotes the value of θ evaluated at E_F.

Combination of the above results enables us to find the density at all points.

2. Two Turning Points

Another common situation involves two turning points a and b, such as shown in Fig. 6. In the vicinity of each, the density is quite well described by the single turning point theory of the last section. However, it is quite straightforward to develop a formalism which describes the simultaneous effect of both turning points over the entire x axis.

In this case, in which the number of electrons N remains finite, the Green's function has discrete poles given by

$$\Theta(E)\equiv\theta(a(E),b(E);E)=(n+\tfrac{1}{2})\pi. \tag{3.23}$$

The contour C, of Fig. 1, may cross the real E axis at any point E_F between the Nth and $(N+1)$th pole. The most convenient choice of E_F is

$$\Theta(E_F)=N\pi. \tag{3.24}$$

The Green's function for this case is given by

$$G(x,x';E)=\frac{\pi}{6}\left[\frac{\theta(a,x)\theta(a,x')}{p(x)p(x')}\right]^{1/2}[J_{1/3}(\theta(a,x))+J_{-1/3}(\theta(a,x))][\sqrt{3}\{J_{1/3}(\theta(a,x'))-J_{-1/3}(\theta(a,x'))\}$$
$$-\tan\Theta(E)\{J_{1/3}(\theta(a,x'))+J_{-1/3}(\theta(a,x'))\}],\quad\text{for}\quad x\leq x', \tag{3.25}$$

or by a similar expression with $\theta(a,x)$ and $\theta(a,x')$ replaced, respectively, by $\theta(x,b)$ and $\theta(x',b)$.

With the choice (3.24) for E_F, $n(x)$ is given exactly by the expressions of the last section, except in the "asymptotic" region III between a_F and b_F (see Fig. 6), in which

$$\begin{aligned} |x-a_F|&\gg\left|\frac{dv}{dx}\right|_{x=a_F}^{-1/3}; \\ |x-b_F|&\gg\left|\frac{dv}{dx}\right|_{x=b_F}^{-1/3}. \end{aligned} \tag{3.26}$$

In this region one finds

$$G(x;E)=-(1/2p)[\tan\Theta+(\cos(\theta_1-\theta_2)/\cos\Theta)], \tag{3.27}$$

where

$$\theta_1\equiv\theta(a(E),x;E);\quad\theta_2\equiv\theta(x,b(E);E). \tag{3.28}$$

We begin by evaluating the contribution of the first term in (3.27). As one moves upward from E_F on line l (Fig. 5), $\tan\Theta$ rapidly approaches its limiting value i. We therefore expand Θ in powers of $\zeta(=\mathrm{Im}E)$,

$$\Theta=N\pi+i(\mathrm{T}/2)\zeta+\cdots, \tag{3.29}$$

where

$$\mathrm{T}\equiv\int_{a_F}^{b_F}\frac{dt}{(E_F-v(t))^{1/2}}. \tag{3.30}$$

This gives

$$\frac{1}{2\pi i}\oint_c\left[-\frac{1}{2p}\tan\Theta\right]dE-n_0(x)=\mathrm{Re}\left(-\frac{1}{2\pi p(x,E_F)}\right)(-1)^N\int_0^\infty\left(\tanh\frac{\mathrm{T}\zeta}{2}-1\right)id\zeta \tag{3.31}$$
$$=0.$$

Turning now to the second term in (3.27) we write

$$\theta_j=\theta_{j,F}+i(\tau_{j,F}/2)\zeta+\cdots,\quad j=1,2, \tag{3.32}$$

where the subscript F implies $E=E_F$ and

$$\tau_{1,F}=\tau(a_F,x;E_F);\quad \tau_{2,F}=\tau(x,b_F;E_F). \tag{3.33}$$

For the upper half of l, we rewrite the contour integral by changing the variable ζ to

$$s=e^{-T\zeta}, \tag{3.34}$$

giving us

$$\int_0^\infty d\zeta\frac{\cos(\theta_1-\theta_2)}{\cos\Theta}=\frac{(-1)_N}{\mathrm{T}}\left[e^{i(\theta_{1,F}-\theta_{2,F})}\int_0^1(s^{(\mathrm{T}+\tau_{1,F}-\tau_{2,F}/2\mathrm{T})-1}/1+s)ds\right.$$
$$\left.+e^{i(\theta_{2,F}-\theta_{1,F})}\int_0^1(s^{(\mathrm{T}+\tau_{2,F}-\tau_{1,F}/2\mathrm{T})-1}/1+s)ds\right]. \tag{3.35}$$

Hence, the quantum density oscillations are given by

$$n'(x)\equiv\frac{1}{2\pi i}\oint_c\left\{-\frac{1}{2p}\frac{\cos(\theta_1-\theta_2)}{\cos(\Theta)}\right\}dE$$
$$=(-1)^{N+1}\frac{\cos(\theta_{1,F}-\theta_{2,F})}{\pi p(x,E_F)}\left[\frac{1}{\mathrm{T}+\tau_{1,F}-\tau_{2,F}}\,{}_2F_1\left(1,\frac{\mathrm{T}+\tau_{1,F}-\tau_{2,F}}{2\mathrm{T}};1+\frac{\mathrm{T}+\tau_{1,F}-\tau_{2,F}}{2\mathrm{T}};-1\right)\right.$$
$$\left.+\frac{1}{\mathrm{T}+\tau_{2,F}-\tau_{1,F}}\,{}_2F_1\left(1,\frac{\mathrm{T}+\tau_{2,F}-\tau_{1,F}}{2\mathrm{T}};1+\frac{\mathrm{T}+\tau_{2,F}-\tau_{1,F}}{2\mathrm{T}};-1\right)\right], \tag{3.36}$$

where ${}_2F_1$ denotes a hypergeometric function.[10]

The results of this section have been applied to two examples. The first is the oscillator potential with $N=2$ and 11. In both cases, the present theory reproduces the exact density, including the quantum density oscillations, within a few per cent (Appendix 2).

The other example is a system of non-interacting electrons in a three-dimensional unscreened Coulomb potential with quantum numbers corresponding to barium. By means of a transformation of variables[7] the radial equations are transformed to problems with two turning points which can then be treated by the methods of this section (Appendix 3).

APPENDIX 1. DISTURBANCE IN A SLOWLY VARYING MEDIUM

As an illustration of the methods developed in Sec. II.1, we have worked out the density changes produced by an infinitesimal δ-function potential, perturbing an electron gas in a slowly varying linear potential. The total potential of our system was taken as

$$v(x)=cx+\lambda\delta(x), \tag{A1.1}$$

with $c=0.05$ and λ infinitesimal. E_F was chosen as 1.0. The corresponding density is by Eq. (2.1),

$$n(x)=n^s(x)+\lambda\alpha(0,x), \tag{A1.2}$$

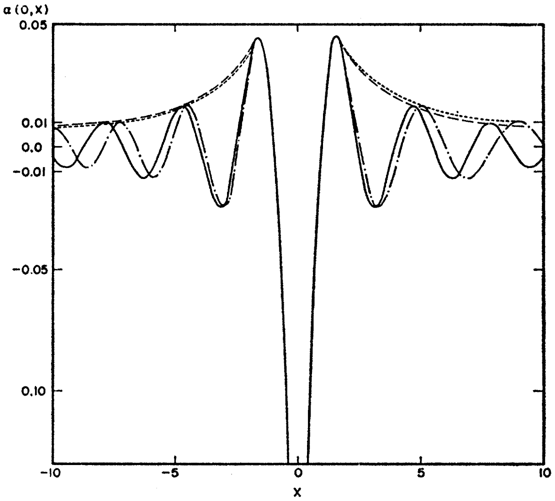

FIG. 7. Polarizabilities in a uniform electron gas [—— $\alpha_0(0,x)$] and in a linear potential [—·—·—·— $\alpha(0,x)$].

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[10] *Bateman Manuscript Project*, edited by H. Erdelyi (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 1, p. 20.

where by Eq. (2.8),

$$\alpha(0,x) = -\frac{1}{6\pi}\frac{(E_F-cx)^{3/2}-E_F{}^{3/2}}{[(E_F-cx)^{1/2}-E_F{}^{1/2}](E_F-cx)^{1/2}E_F{}^{1/2}} \times\left\{\frac{\pi}{2}-\mathrm{Si}\left[\frac{4}{3c}(E_F{}^{3/2}-(E_F-cx)^{3/2})\right]\right\}. \quad \text{(A1.3)}$$

This quantity is plotted in Fig. 7, where it is compared with the polarizability $\alpha_0(0,x)$ of a uniform gas ($c=0$). It will be noticed that for positive x, where the background density n^s is decreasing, the "wavelength" and amplitude of $\alpha(0,x)$ exceed those of $\alpha_0(0,x)$, while for negative x the opposite is the case.

APPENDIX 2. ELECTRON DENSITY IN A HARMONIC OSCILLATOR POTENTIAL

This Appendix is an illustration of Sec. III. We consider electrons described by the Schrödinger equation

$$-(d^2\psi/dx^2)+(x^2-E)\psi=0. \quad \text{(A2.1)}$$

For this system all quantities needed in Eqs. (3.19), (3.22) and (3.36) can be easily evaluated. The resulting densities for 2 and 11 electrons are shown in Fig. 8.

It will be seen that the Thomas-Fermi density, $n^s(x)$ (without any gradient corrections[1]), corresponds quite well to a smoothed average of the actual density. When the quantum corrections $n'(x)$, appropriate to the various regions, are added, one obtains a remarkably close agreement with the exact density, even for only two occupied levels.[11]

APPENDIX 3. ELECTRON DENSITY IN A COULOMB POTENTIAL

This forms another illustration of Sec. III. Because of the spherical symmetry of the Coulomb potential, we can separate the Schrödinger equation for the wave function and hence that for the Green's function and consider only the "reduced" radial parts, $R_l(r,E)$ and $G_l(r,r';E)$, with angular momentum quantum number l, satisfying, respectively, the equations,

$$[-(d^2/dr^2)+\{v(r)+[l(l+1)/r^2]-E\}] \times R_l(r,E)=0, \quad \text{(A3.1)}$$

$$[-(d^2/dr^2)+\{v(r)+[l(l+1)/r^2]-E\}] \times G_l(r,r';E)=-\delta(r-r'), \quad \text{(A3.2)}$$

where $v(r)$ is the Coulomb potential $-(2/r)$. The radial density functions are given by

$$n_l(r)=\sum_n |R_l(r,E_{nl})|^2=\frac{1}{2\pi i}\oint_C dE\, G_l(r;E), \quad \text{(A3.3)}$$

where E_{nl} denote the eigenvalues of (A3.1) and C is the contour in E plane enclosing occupied E_{nl} for a particular l.

Although (A3.1) resembles a one-dimensional Schrödinger equation with an effective potential

$$v(r)+[l(l+1)/r^2],$$

we cannot apply the methods developed above to this equation because of the singularity of $v(r)+[l(l+1)/r^2]$ at $r=0$. However, if a transformation due to Langer[7] is applied, namely,

$$r=e^x, \quad R(r)=e^{x/2}\varphi(x), \quad \text{(A3.4)}$$

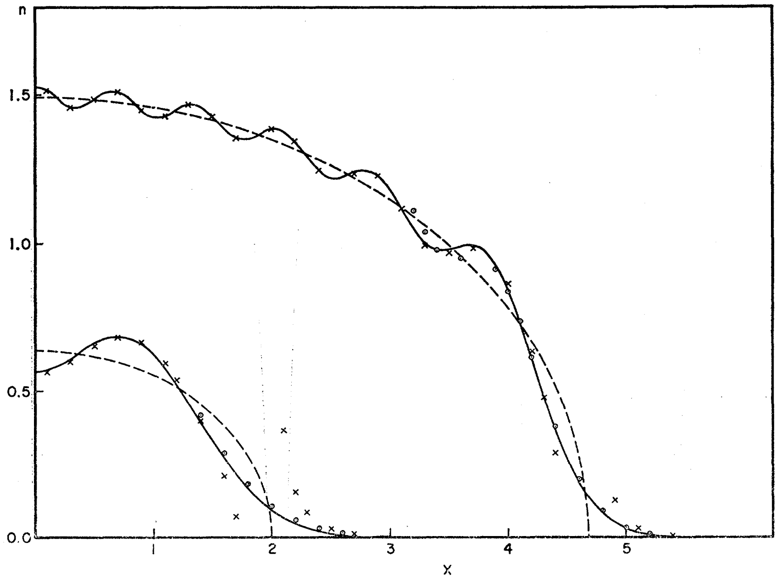

FIG. 8. Electron density in a harmonic potential well. —— Exact. ---- Thomas-Fermi approximation. ×× Approximate formulas (3.19) and (3.36) away from the turning points. ⊙ Formula (3.22) near the turning points.

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[11] For references of earlier works relating to this example, see N. H. March, Advan. Phys. 6, 1 (1957).

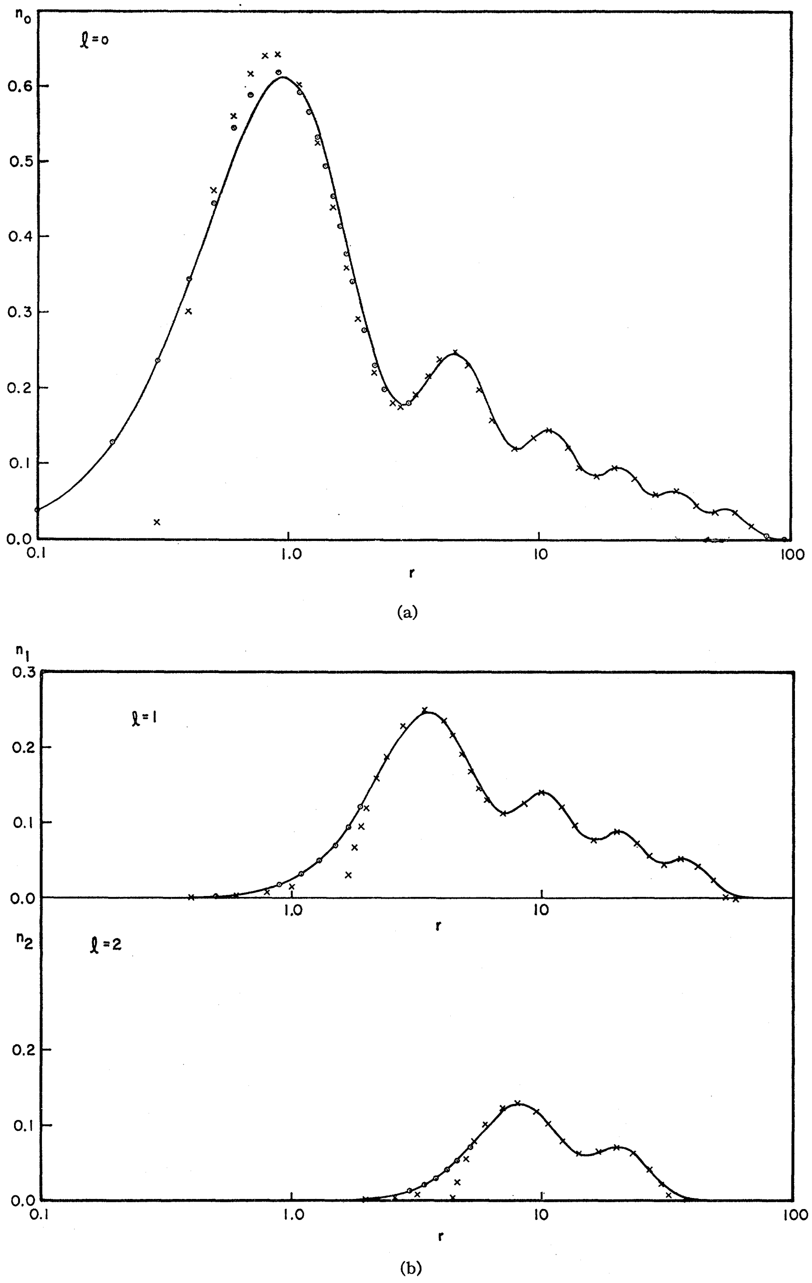

FIG. 9. Electron densities for various angular momenta in a Coulomb potential. —— Exact. ×× Approximate formulas (3.19) and (3.36) away from the turning points. ⊙ The turning point regions.

Eq. (A3.1) becomes

$$(d^2\varphi_l/dx^2)+q_l^2(x)\varphi_l=0\,, \qquad \text{(A3.5)}$$

where

$$q_l^2(x)=\{E-v(e^x)\}e^{2x}-(l+\tfrac{1}{2})^2. \qquad \text{(A3.6)}$$

The function $q_l^2(x)$ is free of singularities. (A3.5) is not exactly a Schrödinger-type equation; nevertheless methods of Sec. III can be applied with turning points now defined as the two values of x where $q_l^2(x)$ vanishes.

There are no difficulties except for the region near the left turning point. For values of x in this region, the Green's function along the straight line portion of the contour C in Fig. 5 does not approach the asymptotic value rapidly enough for the linear potential approximation (3.20) to be adequate. This trouble is most pronounced for $l=0$ and diminishes rapidly as l increases. Thus, for the computation of the density $n_l(r)$ for $l=0$, we are forced to integrate the Green's function numerically along the straight line portion of C instead of using (3.22).

In Fig. 9, we present the approximate and exact radial densities for singly occupied levels up to 6s, 5p, and 4d, respectively. It will be seen that there is good agreement.