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Edge confinement of a two-dimensional electron gas and its relevance to the electron density near a vacancy defect in graphite

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Motivated by electron-tunnelling microscopy showing enhancement of electron density near the HOMO level in graphite, we present an analytical solution for the density in a two-dimensional free-electron assembly subject to edge confinement. In fact starting from the so-called Slater sum of statistical mechanics, the general result for arbitrary dimension d is obtained for this electron gas model.

1. Background and outline

The motivation for the present study resides in recent experiments using scanning tunnelling microscopy techniques to study the density of the π-electrons near a graphitic edge [1,2] or around a graphitic vacancy defect [3,4]. On physical grounds, we expect, using the underlying philosophy of density functional theory, that the enhancement of electron density near the HOMO level observed outside a vacancy cell can be described as a result of a strong repulsive potential representing the defect. And a similar comment applies for the electron density enhancement sometimes seen near a graphite edge.

In constructing an admittedly oversimplified defect model giving the gist of the experiments cited above, we have appealed to earlier investigations involving one of us [5,6] in which the electron density around a vacancy in Al was compared with that of electrons spilling out of a planar Al surface [7]. The two electron densities proved to be graphically indistinguishable. It is this observation, together with the relation demonstrated by March [6] between vacancy formation energy and surface energy, that has led us to construct the 'edge confinement' model of a two-dimensional electron gas solved in the present paper.

With the above as background, the outline of the work is as follows. In section 2 immediately below, known results are summarized for one- and three-dimensional electron gases confined by an infinite barrier. It is there pointed out that these two electron densities are special cases of a d-dimensional result, for d odd (see also [8]). Section 3

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is concerned with the present model, namely edge confinement of a two-dimensional electron gas, the confinement again being 'mimicked' by an infinite potential barrier. After solving the two-dimensional case, it is shown that the result is readily generalized to d dimensions, with d now restricted to be even. Contact with the experimental observations in graphite is then established in section 4, while section 5 constitutes a summary.

2. Infinite barrier confinement of one- and three-dimensional electron gases

As an introduction to the present model, it is instructive to start from the simplest undergraduate problem in quantum mechanics; namely, electrons confined in a one-dimensional box between $z = 0$ and $z = l$. Singly filling the lowest N levels, one obtains from the (standing) normalized wave functions $\psi_n = (2/l)^{1/2}\sin(n\pi z/l)$ the electron density $\rho_1(z)$ as

$$\rho_1(z) = \sum_{n=1}^{N}\left(\frac{2}{l}\right)\sin^2\left(\frac{n\pi z}{l}\right). \tag{2.1}$$

The summation in equation (2.1) can be developed exactly as the ratio of two sine functions, and yields

$$\rho_1(z) = \frac{2N+1}{2l} - \frac{1}{2l}\frac{\sin((2N+1)\pi z/l)}{\sin(\pi z/l)}. \tag{2.2}$$

To achieve the desired electron gas confinement, we now take the limit in equation (2.2) as the length of the box l tends to infinity, to find

$$\rho_1(z)\big|_{l\to\infty} = \rho_{10}\left[1 - \frac{\sin(2k_F z)}{2k_F z}\right], \tag{2.3}$$

where the constant density ρ_{10} (actually number of electrons/unit length) is simply N/l as $N \to \infty$, $l \to \infty$, N/l finite, while the Fermi wave number k_F is given in terms of ρ_{10} by the 'phase space' result that a cell of size h can hold one electron (for the singly filled case under discussion, or two for spin compensation); i.e.,

$$\rho_{10} \equiv \frac{N}{l} = \frac{2\hbar k_F}{h} = \frac{k_F}{\pi}, \tag{2.4}$$

since $2\hbar k_F$ is the extent of the occupied region in momentum space. In the language used below, equation (2.3) represents the density $\rho_1(z)$ of 'point' confinement of an electron gas by an infinite barrier at $z = 0$. For a general energy E up to which the levels are filled, equation (2.3) can be immediately generalized to yield

$$\rho_1(z, E) = \frac{\sqrt{2mE}}{\pi\hbar} - \frac{1}{2\pi z}\sin\left(\frac{2^{3/2}\sqrt{mE}z}{\hbar}\right). \tag{2.5}$$

For reasons which will emerge below, the local density of states $\partial\rho_1/\partial E$ will also be a major interest here, and is given in this one-dimensional model as

$$\frac{\partial\rho_1(z,E)}{\partial E} = \sqrt{\frac{m}{2}}\frac{E^{-1/2}}{\pi\hbar}\left[1-\cos\left(2^{3/2}\frac{\sqrt{mE}}{\hbar}z\right)\right]. \tag{2.6}$$

The first term on the right-hand side of equation (2.6) is simply the (constant, i.e., z-independent) density of states of a one-dimensional uniform electron gas. The 'point' confinement causes, of course, a major change near the barrier at $z = 0$, and an oscillatory, undamped correction far from the barrier.

It was Bardeen [9] who gave the theory of confinement of a three-dimensional electron gas by a planar surface represented by an infinite barrier in the x, y plane, placed again at $z = 0$. His result, in an obvious notation, yields the three-dimensional analogue of equation (2.3), as

$$\rho_3(z) = \rho_{30}\left[1-\frac{3j_1(2k_Fz)}{2k_Fz}\right] \tag{2.7}$$

in which the interrelation is more apparent if one notes that $\sin(2k_Fz)/2k_Fz = j_0(2k_Fz)$ and $j_1(x) = (\sin x - x\cos x)/x^2$, with $j_n(x)$ the nth-order spherical Bessel function. For singly occupied levels,

$$\rho_{30} = \frac{k_F^3}{6\pi^2}. \tag{2.8}$$

In the language of metal physics, the oscillations in $\rho_3(z)$ at large z are now known as Friedel oscillations [10,11], and though the arguments of Friedel et al. [10] were applicable to more general 'perturbing potentials' in a three-dimensional electron gas, these oscillations were already plain in the 1936 work of Bardeen on planar surface confinement. One of us [8] subsequently gave a generalization, embracing equations (2.3) and (2.7), to d dimensions, with d odd, $j_{(d-1)/2}(x)$ being the order of the spherical Bessel function in the general case for d odd.

With this summary of earlier results, we turn to the main focus of the present study, namely, edge confinement of a two-dimensional electron gas.

3. Edge confinement of a two-dimensional electron gas

We shall solve for the two-dimensional analogue of equations (2.3) and (2.7) via the so-called Slater sum. For eigenfunctions $\psi_i(\mathbf{r})$, with corresponding eigenvalues ε_i, the Slater sum $Z(\mathbf{r},\beta)$ in statistical mechanics is defined by

$$Z(\mathbf{r},\beta) = \sum_{\text{all } i}\psi_i^*(\mathbf{r})\psi_i(\mathbf{r})\exp(-\beta\varepsilon_i), \quad \beta = (k_BT)^{-1}, \tag{3.1}$$

where T is the absolute temperature and k_B is Boltzmann's constant. As utilized in the early work of March and Murray [12], the Slater sum is related to the desired electron density $\rho(\mathbf{r}, E)$ by

$$Z(\mathbf{r},\beta) = \beta \int_0^\infty \rho(\mathbf{r}, E) \exp(-\beta E)\, \mathrm{d}E. \tag{3.2}$$

For one dimension, we can immediately use the result (2.5) to obtain $Z_1(z, \beta)$ as

$$Z_1(z, \beta) = \left(\frac{m}{2\pi \hbar^2 \beta}\right)^{1/2} \left[1 - \exp\left(-\frac{2mz^2}{\hbar^2 \beta}\right)\right]. \tag{3.3}$$

As noted in [8], the d-dimensional Slater sum can be readily obtained from Z_1 as

$$Z_d(z, \beta) = \left(\frac{m}{2\pi \hbar^2 \beta}\right)^{(d-1)/2} Z_1(z, \beta). \tag{3.4}$$

March [8] obtained, by the inverse Laplace transform of $Z_d(z, \beta)/\beta$, the general result for d odd, which can be written in the form

$$\rho_d(z) = \frac{k_F^d}{\pi^{(d+1)/2}} \frac{1}{2^{(d-1)/2}} \left\{ \frac{1}{d!!} - \frac{j_{(d-1)/2}(2k_F z)}{(2k_F z)^{(d-1)/2}} \right\} \tag{3.5}$$

where $d!! = (1 \cdot 3 \cdot 5 \cdots d)$. This expression, of course, embraces the results for ρ_1 and ρ_3 already given above.

We proceed immediately to utilize equation (3.2), plus equation (3.4) for $d = 2$, to construct the electron density $\rho_2(z, E)$ for edge confinement of a two-dimensional electron gas. We have

$$\frac{Z_2}{\beta} = \left(\frac{m}{2\pi \hbar^2 \beta^2}\right) \left[1 - \exp\left(-\frac{2mz^2}{\hbar^2 \beta}\right)\right], \tag{3.6}$$

and therefore using the inverse Laplace transform we find

$$\rho_2(z, E) = \frac{mE}{\hbar^2 \pi} \left[\frac{1}{2} - \frac{J_1(2^{3/2} z (mE/\hbar^2)^{1/2})}{(2^{3/2} z (mE/\hbar^2)^{1/2})}\right], \tag{3.7}$$

where $J_n(x)$ denotes the nth order (ordinary) Bessel function. In the more general case of d even, we can also evaluate the inverse transform; using again equations (3.2) and (3.4), we have

$$\rho_d(z) = \frac{1}{(2\pi)^{d/2}} \left[\frac{(mE/\hbar^2)^{d/2}}{(d/2)!} - \left(\frac{mE}{2\hbar^2 z^2}\right)^{d/4} J_{d/2}\left(2^{3/2} z \left(mE/\hbar^2\right)^{1/2}\right)\right]. \tag{3.8}$$

4. Relevance to vacancy defect in graphite

Figure 1 shows the total electron density $\rho_2(z, E)$, divided by E, versus $z\sqrt{E}$ for the edge-confined two-dimensional electron gas. There is seen to be substantial enhance-

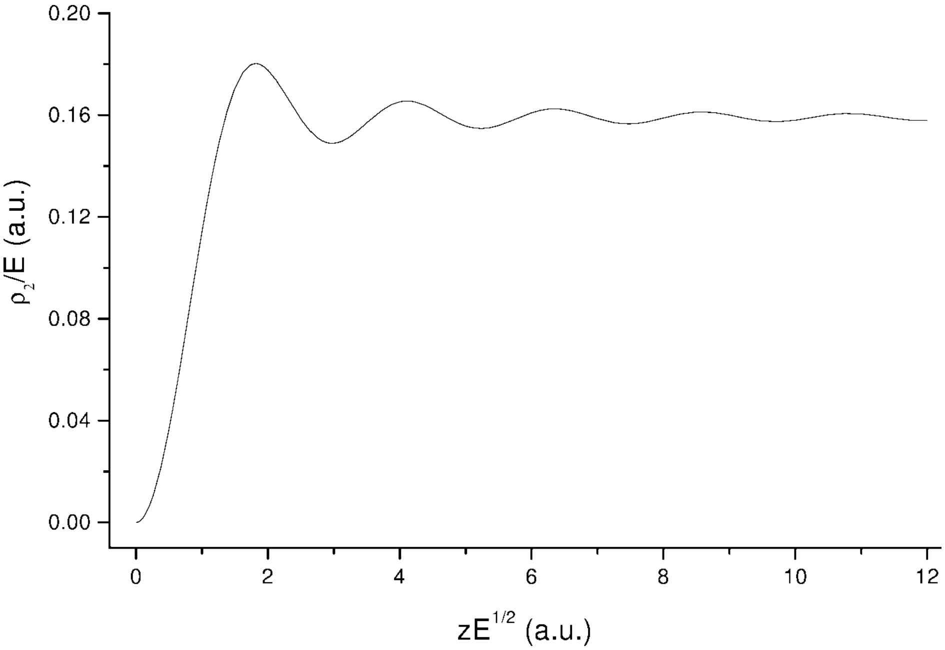

Figure 1. Density $\rho_2(z, E)$ for edge confinement of two-dimensional electron gas. Quantity plotted on ordinate is $\rho_2(z, E)/E$ while abscissa is $z\sqrt{E}$.

ment of ρ_2 over its bulk density value (limit as $z \to \infty$) near the vacancy cell, which is in general accord with the microscopy observation. However, scanning tunnelling microscopy does not sample the whole density, but, e.g., as discussed in [13,14], the part of the electron density contributed by the (occupied) levels nearer the Fermi level is rather more important (and in a manner dependent on the voltage settings of the electron microscope). Thus beyond the total density, the local density due to levels near the HOMO level is relevant. This is given by

$$\frac{\partial \rho_2}{\partial E} = \frac{m}{2\pi\hbar^2}\left[1 - J_0\left(2^{3/2} z \left(\frac{mE}{\hbar^2}\right)^{1/2}\right)\right], \tag{4.1}$$

and a sample plot of this is shown in figure 2. The ‘enhancement’ referred to above is now evidently more pronounced, and effects go out further beyond the vacancy cell. Of course, in this discussion, we are working by analogy with the Al metal case cited earlier by assuming that the ‘vacancy hole’ in a graphite layer is already usefully modelled by edge confinement (the analogue of a planar surface in three dimensions).

5. Summary

The main results of the present study are embodied in equation (3.7) for the edge-confined density $\rho_2(z, E)$, and in figures 1 and 2 for this density and the associated local

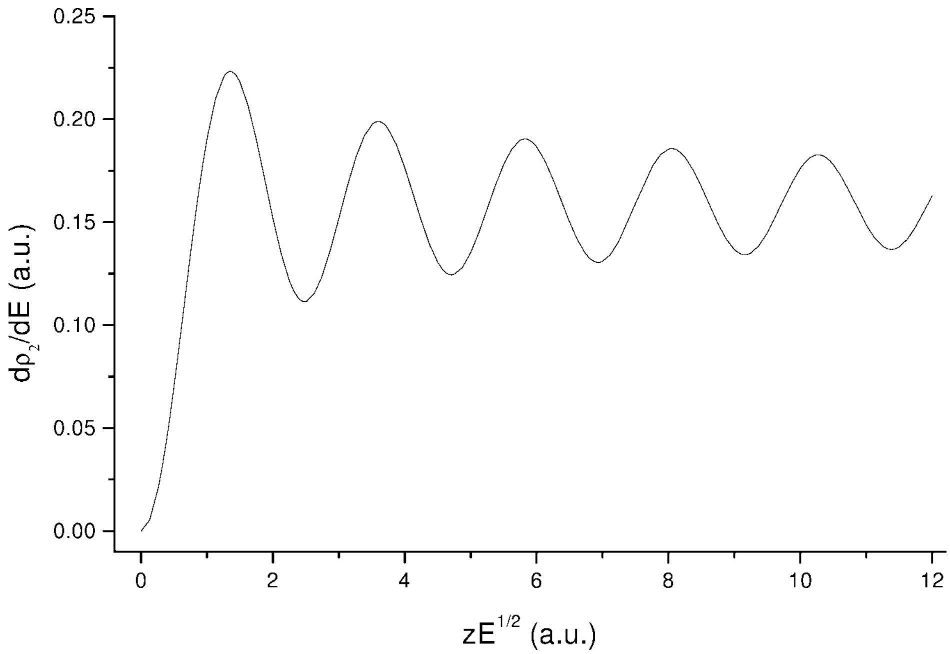

Figure 2. Local density of states $\partial\rho_2(z, E)/\partial E$ versus $z\sqrt{E}$, as derived by differentiation of equation (3.7).

density of states respectively. The latter quantity is most relevant to the microscopy experiments on the vacancy in graphite. While an admittedly simplistic model, the present treatment reveals enhancement of the (π-electron) density in the vicinity of an edge or of a vacancy defect. More elaborate tight-binding models evidently can display [15,16] similar effects, at least for suitable vacancy defects and suitable edges.

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