Electrons, Holes, and the Hall Effect in Amorphous Silicon.*

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The double sign anomaly in hydrogenated amorphous silicon, observed by LeComber et al. [1] in 1977, has remained puzzling ever since. Recently we attacked this problem from two different directions using the equation-of-motion method. Calculations reproduce the double sign anomaly and were rationalised in terms of the behaviour of the spectral function. In a new type of calculation the motion of a 'wave packet' was studied in an applied field. Behaviour characteristic of positive and negative effective masses was found in the same ranges of energy for crystalline and a-Si. A perturbation theory is given for reconciling these results.

The concept of electrons and holes and the effective mass theorem is of enormous importance in simplifying the description of crystalline semiconductors and semiconductor devices. It is not of course necessary to invoke the concept of a hole. One may just as easily work with electrons of negative mass or group velocity and for our present purpose we will discuss electrons in the conduction band and electrons in the valence band. In crystalline semiconductors the Hall coefficient \( R_H \) is an invaluable tool for characterising materials yet in amorphous semiconductors there are few measurements because the results are anomalous in hydrogenated Si (a-Si:H) [1] and the sign of \( R_H \) is usually negative in chalcogenide glasses [2]. In recent years it has become possible to construct quite large models of the archetypal amorphous semiconductors Si and Si:H [3,4] and study the associated electronic properties [5,6,7,8,9]. Perhaps it is important to point out that the use of pseudopotentials [6,10] and a simple tight binding scheme give very similar results. The precise position and notion of band minima and maxima is not crucial in an amorphous structure and it is useful to be able to use a simple tight binding scheme which leads to swift computations for large models.

The use of plane waves and pseudopotentials, however, has one very important aspect. It enables us to construct the spectral function most easily and enquire what remnants of a 'band structure' persist in the amorphous state. The spectral function \( \rho(kE) \) gives the probability of finding an electron with energy \( E \) and wave vector \( k \). For free electrons \( \rho(kE) = \delta(E - k^2) \) (using atomic units) and in a-Si one finds a broadened delta function following the free electron curve up to the band gap essentially at \( k_F \) where \( k_F \) is the free electron Fermi vector. A curious but definite point is that the spectral function narrows near the band edge (although the number of states vanishes). The spectral function tells one nothing about the localisation of states so that this does not mean that \( k \) has become a good quantum number. As one moves into the conduction band the spectral function is again narrow (near \( k_F \)) but rapidly broadens. The average value of \( k \) (\( \bar{k} \)) moves back towards \( k=0 \) but then continues on in a roughly free electron like fashion. The concepts of direct and indirect gaps have no significance in the light of such behaviour. The point of these remarks is to stress that the behaviour

\[
E = E_c + \beta_c(k_c - \bar{k})^{1/2}, \quad E > E_c, \quad k_c > \bar{k}
\]

\[
E = E_v - \beta_v(k_v - \bar{k})^{1/2}, \quad E < E_v, \quad k_v > \bar{k}
\]  

(1)

describe the density of states close to the band edges because of the narrowness of the spectral function. \( E_c \) and \( E_v \) denote the conduction and valence band edges respectively, \( \beta_c \) and \( \beta_v \) are positive and \( k_c \approx k_v \approx k_F \) [7]. The main purpose of these remarks are to preface later speculation as to whether or not an 'effective mass' theorem could exist for amorphous Si and to point out that

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when the states are not localised the sign of $\frac{dE}{dk}$ could explain the double sign anomaly in $R_H$.

We now turn to two different computer simulation experiments which relate to this problem of the Hall effect. Both pieces of work utilise the equation of motion method [7,11] and a filtering technique which enables one to pick out eigenstates in a narrow range of energy. In the first of these studies we evaluated the Kubo formula for the Hall conductivity ($\sigma_{xy}$) on either side of the gap (Figure 1) as a function of energy. This turned out to be a difficult computation and could only be done on a small model (216 atoms). The results are noisy because $\sigma_{xy}$ is also small in comparison with the ordinary conductivity but there is a clear verification of the double sign anomaly observed by LeComber et al. [1]. It would be difficult to carry out this calculation on a crystal because of the small size of the model and mean free path effects. In the second piece of work electrons within narrow ranges of energy were selected and located near the $z$-$y$ plane down the centre of a 'slab' of a-Si containing atoms. A weak 'field' was then switched on in the x-direction corresponding to modifying the diagonal terms of the tight binding Hamiltonian by $H' = -P\sin(2\pi(x - a/2)/a)$ where $a/2$ is the centre of the slab and $x$ is the position of a Si atom. Periodic boundary conditions are applied in all directions. The argument is that provided the initial distribution of electrons does not diffuse too rapidly the motion should correspond to the motion in a 'field' $-e^2 P2\pi/a$. The 'centre of gravity' of the distribution as a function of time is shown in Figure 2 for electrons at the edge of the conduction and valence band relative to the centre of the slab at $a/2$. The direction of the motion of electrons is exactly the same for crystalline Si although the details of the time dependence differ [11]. Can these results be reconciled? The first point is that the motion of the valence and conduction electrons can not correspond to electrical conductivity. Charge always moves in the same direction, namely the conductivity is always positive. Before explaining the behaviour using a perturbation argument let us remember that for crystals a local potential which is, say, attractive to electrons in the conduction band is repulsive to electrons in the valence band using the effective mass theorem. Let us replace $H'$ by a 'saw tooth' potential namely, $H' = -P2\pi(x - a/2)/a$, but still retain periodic boundary conditions so that the results shown in Figure 2 hardly change. If we assume that the eigenstates $\psi_n^0$ are distributed uniformly, on the average, across the sample then to lowest order in $H'$ the expectation value $(x - a/2)_{mn}$ is given by

$$\langle x - a/2 \rangle_{mn} \simeq -2P\frac{2\pi}{a} \sum_m \frac{\langle n| x - a/2|m \rangle^2}{E_n^0 - E_m^0} \quad (2)$$

where $E_n^0$ denotes an unperturbed eigenvalue.

The field applied by Weaire and Hobbs [11] was weak. Since the matrix elements $\langle |M|^2 \rangle$ are positive definite we can estimate (2) treating $|M|^2$ as roughly constant so that, as a function of energy ($E$)

$$\langle x - a/2 \rangle \simeq -2P\frac{2\pi}{a} |M|^2 \int g(E')\left(E - E'\right)^2 + \xi^2 \quad (3)$$

where $\xi$ is an infinitesimal and $g(E)$ is the density of states. This integral changes sign at the band gap and the sign changes agree with those observed by Weaire and Hobbs at other energies. There is not much difference in the density of states in a-Si and c-Si and since $g(E)$ occurs in a principal part integral it is hardly surprising that there is similar behaviour in the movement produced by $H'$.

The above simple argument prompted consideration of an alternative argument for the behaviour of $\sigma_{xy}$. There are many different forms for $\sigma_{xy}$ but one in particular derived by Morgan and Howson [12] is as follows

$$\sigma_{xy} = \frac{4e^2\hbar^2}{\Omega\pi} Tr(A + B) \quad (4)$$

where

$$A = V^* G_I V^* G_R V^* G_I V^* G_I, \quad B = V^* G_I V^* G_I V^* G_R V^* G_I$$

and the important thing is that $G_I$, which is the imaginary part of the Green function, gives something like the density of states while the real part
$G_R$ gives principal integrals which can clearly produce sign changes. Equation (4) has been evaluated using the random phase model (r.p.m.) [13] and this is also plotted in Figure 1. The qualitative agreement is excellent considering the crudity of the r.p.m.

Finally, it is interesting to speculate on the possibility of an effective mass theorem for amorphous Si. In a crystalline semiconductor there is a unique wave function associated with each energy maximum or minimum. The effective mass wave functions are then modulated forms of these extremal states. Clearly this is not possible in an ideal fully bonded amorphous semiconductor with a clear gap where there will be one state closest to the band edge which will be localised in some region of space. However the relations in equation (1) refer to the propagation of an average or coherent part of a wave amplitude. If we consider the conduction band and set $E_c = 0$ then we might consider replacing $k$ by $i^{-1}V$ in the spirit of the effective mass approximation but this would give a clumsy looking equation. Let us next consider

$$\beta_c^2 (k_c - k) \psi = E^2 \psi$$  \hspace{1cm} (5)

and then for $k$ near to $k_c$ write this as

$$\frac{\beta_c^2}{2k_c} (k_c^2 - k^2) \psi + V (E - V) \psi \simeq E (E - V) \psi$$ \hspace{1cm} (6)

where the effect of an additional potential $V(r)$ has been added in, ignoring derivatives of $V(r)$ when it varies slowly. We then arrive at the equation $(E < 0)$

$$-\frac{\beta_c^2}{2k_c |E|} \nabla^2 \psi + 2V(r)\psi - \frac{V^2(r)}{|E|} \psi \simeq -(|E| - \frac{\beta_c^2 k_c}{2|E|}) \psi$$ \hspace{1cm} (7)

with an effective mass $m^* = \frac{k_c \hbar^2 |E|}{\beta_c^2}$. It is difficult to estimate $\beta_c$ from numerical calculations of the density of states because the forms in (1) are only supposed to be valid very close to the band edges. We can however ask about the effect of the finite thickness of amorphous Si films on the band gap as observed in the measurements of Abeles and Tiedje [14] on amorphous semiconductor superlattices. For a film of thickness $a$ in the x-direction the energy levels are given by

$$E_c^n = E_c + \left(\frac{\beta_c^2}{2k_c} (k_c^2 - k^2) - \left(\frac{n\pi}{a}\right)^2\right)^{1/2}$$

$$E_v^n = E_v + \left(\frac{\beta_c^2}{2k_v} (k_v^2 - k^2) - \left(\frac{n\pi}{a}\right)^2\right)^{1/2}$$ \hspace{1cm} (8)

where $n$ is a positive integer and $k_{\perp}$ denotes a wave vector in the $y,z$ plane. These results are obtained by solving (7) with $\psi = 0$ at $x=0$ and $x=a$. The behaviour of the density of states at the conduction band edges will clearly be modified because the allowed values of $n$ will be restricted for small values of $a$ in order to keep the square roots real. It is not clear at the present time if this behaviour can explain the results of Abeles and Tiedje but the important thing to note is that confinement of the electronic states can affect the behaviour at the band edge.

We can now return to (7) for a singly charged substitutional donor atom and calculate the binding energy $\Delta E$. This is simple if we ignore the $V^2$ term because (7) can be cast in the form of a hydrogenic-like equation to give the binding energy

$$\Delta E_n \simeq \left(\frac{\beta_c}{2} \left(1 - \frac{4k_c}{n^2 \epsilon_r \beta_c^2}\right)^{-1}\right)^{1/3}$$ \hspace{1cm} (9)

where $n$ is an integer and $\epsilon_r$ is a dielectric constant. The curious thing about this result is that bounded states become deeper with increasing $n$ as the effective mass is energy dependent.

In general both band edges should be incorporated into the argument when there are deep states. This may be achieved for example (taking $\beta_c = \beta_v$ and $k_c = k_v$) by writing $E^2 = (E_v / 2)^2 + \alpha (k_c - k)^2$ where $E_v$ is the energy gap. However the basic argument appears sound and could be modified for different behaviour to that given in (1), for example if the exponent 1/2 is changed to 2/3 the density of states would be proportional to the square root of $(E - E_c)$ and $(E_v - E)$ for which there is some evidence[15]. The case of bound donor or acceptor states is clearly a complex one but equation (7) shows how electrons at the edge of the valence and conduction bands should move in opposite directions due to a local potential and in the same direction as observed in a crystal.
This paper shows how the two different types of computer simulation may be reconciled, namely that the direction of electrons in a local potential need not be the same as in an extended electric or magnetic field.

![Figure 1](image1.png)

**Figure 1.** The Hall conductivity ($\sigma_{xy}$) as a function of energy obtained from the random phase model (continuous line) and from a computer simulation (points with error bars).

The effective mass argument supports the ‘wave packet’ experiment but can also provide an interpretation of the sign of the Hall coefficient.

References