# Holes

**Holes** are the absence of electrons in those energy levels of the valence band that have been vacated by electrons moving up to the conduction band. To see how conductivity works, we need to treat both the electrons that move up to the conduction band and the almost filled valence band. However, we can (and do) treat the almost filled valence band in terms of holes **as if the holes were actual particles** with the following five attributes: momentum (or k); energy, velocity, mass, and charge. An imperfect analogy for holes in the valence band would be bubbles under water where the bubbles are "missing water" under water.

## 1. Wavevector of holes vs electrons

As we have already seen, the wavevector (k) of the electron's wave is related to the momentum of the electron (recall we still must deal with the wave/particle duality of the electron: $\lambda=h/p$ so $k=2\pi/\lambda=2\pi p/h=p/\hbar$)

Let's first consider a filled band: $\Sigma\mathbf{k}_e = 0$ since there are as many states with +k as there are with -k values. Now if we have a missing electron, then the $\Sigma\mathbf{k}_{\text{band with hole}} = \Sigma\mathbf{k}_{\text{full band}} - \mathbf{k}_e = 0 - \mathbf{k}_e = -\mathbf{k}_e$. Thus we can say that the $\mathbf{k}_{\text{hole}} \equiv \Sigma\mathbf{k}_{\text{band with hole}} = -\mathbf{k}_e$. If a hole has momentum to the right, an electron must have momentum to the left to fill in that hole.

## 2. Energy of holes vs electrons

If we **assume that the $\varepsilon=0$ at the top of the (almost) filled valence band** (this is equivalent to saying PE=mgh and choosing h=0 at the "floor"), then it takes energy to move an electron up from the valence band to the conduction band. It also implies that the electrons have negative energy while they are in the valence band (negative energy usually means that the electrons are bound and not free to roam - which is consistent with the difference between valence and conduction electrons). Thus if an electron moves from the valence band up to the conduction band, the valence band then is losing a negative energy, which can also be expresses as the valence band is gaining a positive energy! Thus $\varepsilon_{\text{hole}}(\mathbf{k}_{\text{hole}}) = -\varepsilon_e(\mathbf{k}_e) > 0$ [Here $\varepsilon(\mathbf{k})$ means $\varepsilon$ is a function of $\mathbf{k}$. Remember that energy depends on the square of the momentum and hence k, so $\varepsilon_e(-\mathbf{k}_e) \approx \varepsilon_e(\mathbf{k}_e)$.]

## 3. Velocity of holes vs electrons

How do we work with velocity of a particle if we have the electron behaving as a wave when it goes from one place to another (recall we must always consider the wave/particle duality)? We must work with the group velocity: $\mathbf{v}_{\text{particle}} = \mathbf{v}_{\text{group}} = d\omega/d\mathbf{k}$; but for waves, $\varepsilon = \hbar\omega$; thus we can say: $\mathbf{v}_{\text{particle}} = d(\varepsilon/\hbar)/d\mathbf{k}$, or more generally (in 3-D):

$$\mathbf{v}_{\text{particle}} = (1/\hbar)(\nabla_{\mathbf{k}}\varepsilon), \quad \text{where} \quad \nabla_{\mathbf{k}} = (\partial/\partial k_x)\mathbf{x} + (\partial/\partial k_y)\mathbf{y} + (\partial/\partial k_z)\mathbf{z}.$$

Since $\mathbf{k}_{\text{hole}} = -\mathbf{k}_e$, then $\nabla_{\mathbf{k}\text{-hole}} = -\nabla_{\mathbf{k}\text{-e}}$; also recall that $\varepsilon_{\text{hole}} = -\varepsilon_e$.

$$\mathbf{v}_{\text{hole}} = (1/\hbar)\nabla_{\mathbf{k}\text{-hole}}[\varepsilon_{\text{hole}}] = (1/\hbar)(-\nabla_{\mathbf{k}\text{-e}}[-\varepsilon_e]) = +\mathbf{v}_e.$$

Classically, $KE = \frac{1}{2}mv^2 = p^2/2m$, so $d(KE)/dp = p/m = v$; from quantum, $p=\hbar k$, so $d(KE)/dp = d(KE)/\hbar dk = (1/\hbar)d(KE)/dk = v$.
This doesn't look right, since from 1 above: $\mathbf{k}_{\text{hole}} = -\mathbf{k}_e$. Why didn't we just work with $\hbar\mathbf{k} = \mathbf{p} = m\mathbf{v}$? The reason for both is that we need to consider the $m_e$ versus $m_h$ which we do next.

## 4. Mass of holes vs electrons

Now since $\mathbf{k}_{\text{hole}} = -\mathbf{k}_e$, which leads to $\mathbf{p}_{\text{hole}} = -\mathbf{p}_e$, and $\mathbf{p} = m\mathbf{v}$; and since $\mathbf{v}_{\text{hole}} = \mathbf{v}_e$, then this leads to the strange conclusion that $\mathbf{m}_{\text{hole}} = -\mathbf{m}_e$. But this is not really all that strange since a hole is a "missing" amount of mass from the band!

Below and in the next section we will talk about "effective" mass. In that discussion we will see that **the effective mass of the electrons in the valence band near the band gap is actually negative**! What this means, then, is **that the effective mass of the holes is positive**!

**5. Charge of holes vs electrons (and the equation of motion for holes)**

To see how holes carry charge, let's consider the equation of motion for electrons and then see how it applies for holes. But how do we write an equation of motion ($\Sigma\mathbf{F}=m\mathbf{a}$) in the wave/particle duality scheme? Let's consider force through a distance doing work (and hence increasing energy):

$\delta\varepsilon = \text{Work} = \Sigma\mathbf{F}\bullet\mathbf{ds} = \Sigma\mathbf{F}\bullet\mathbf{v}_{group}\delta t$; but $\delta\varepsilon = (d\varepsilon/d\mathbf{k})\bullet\delta\mathbf{k} = \hbar\mathbf{v_g}\bullet\delta\mathbf{k}$ [since $\mathbf{v_g} = d\omega/d\mathbf{k} = (1/\hbar)d\varepsilon/d\mathbf{k}$)];

therefore we can write: $\Sigma\mathbf{F}\bullet\mathbf{v_g}\delta t = \hbar\mathbf{v_g}\bullet\delta\mathbf{k}$, or $\Sigma\mathbf{F} = \hbar(d\mathbf{k}/dt) = d\mathbf{p}/dt$ ,

just as we had for a free electron.

Now with $\mathbf{F}_{el} = q\mathbf{E}$ and $\mathbf{F}_{mag} = q\mathbf{v}\times\mathbf{B}$ :

$$d\mathbf{p_e}/dt = \hbar(d\mathbf{k}_e/dt) = -e\mathbf{E} + -e\mathbf{v}_e\times\mathbf{B} \quad ;$$

but for a hole: $\mathbf{k}_e = -\mathbf{k}_{hole}$, and $\mathbf{v}_e = \mathbf{v}_{hole}$; so:

$$-\hbar(d\mathbf{k}_{hole}/dt) = -e\mathbf{E} + -e\mathbf{v}_{hole}\times\mathbf{B}$$ , or getting rid of all the minus signs

$$d\mathbf{p_h}/dt = \hbar(d\mathbf{k}_{hole}/dt) = e\mathbf{E} + e\mathbf{v}_{hole}\times\mathbf{B} \quad ;$$

which is the equation of motion of a particle with a positive charge, e! Hence **the hole acts and moves like a positive charge**! This could then explain the positive value of the Hall coefficient for some semiconductors!

## Review of Properties of Holes

1. $\mathbf{k}_{hole} = -\mathbf{k}_e$ (hence momentum of hole is opposite that of electron)
2. $\varepsilon_{hole} = -\varepsilon_e$ (however, $\varepsilon_e$ in valence band is < 0; so $\boldsymbol{\varepsilon_{hole}} > \mathbf{0}$)
3. $\mathbf{v}_{hole} = \mathbf{v}_e$ (velocity of the hole is in the same direction as the electron)
4. $m_{hole} = -m_e$ (however, we shall see that effective mass of the electron in the valence band is less than zero, so $\mathbf{m_{hole}} > \mathbf{0}$.)
5. $d\mathbf{p}_{hole}/dt = \hbar(d\mathbf{k}_{hole}/dt) = +e(\mathbf{E} + \mathbf{v}\times\mathbf{B})$ (equation of motion implies a hole acts just like it has a **positive charge**)

### Momentum of electrons in a periodic lattice

It was fairly straightforward to see how four of the attributes of electrons are related to holes: wavevector, energy, velocity, and equation of motion (and hence charge). However, we need to consider what effect the lattice has on two other attributes of the electron: its momentum and its "effective" mass. These need to be considered since we no longer have free electrons, but rather electrons that are interacting with the lattice. **It would be most convenient if we could treat the electrons and holes as if they were free particles where the effects of the potential due to the ions at the lattice positions could be incorporated by considering the particles to have "effective" masses rather than just the ordinary electronic mass.** We now show how to do this.

From the **quantum theory**, the probability of finding the electron at some position, x, at some time, t, is related to the solution of Schrodinger's Equation, called the wavefunction, ψ, by:
Prob(x,t) = $\psi^*(x,t)*\psi(x,t)$ where $\psi^*$ is the complex conjugate of ψ. The momentum of a particle can be found from the wavefunction, ψ, by using the momentum operator, $\mathbf{p}_{operator} = (-i\hbar\partial/\partial\mathbf{x})$, and performing the operation:

$$\mathbf{p} = \int\{\psi^*(x,t)\mathbf{p}_{operator}\psi(x,t)\}dV = \int\{\psi^*(-i\hbar\partial/\partial\mathbf{x})\psi\}dV .$$

For a **free** electron, $\psi(x,t) = Ae^{-i(E/\hbar)t}e^{ikx}$, so

$$\mathbf{p}_{\text{free electron}} = \int\{(Ae^{i(E/\hbar)t}e^{-ikx})(-i\hbar)(i\mathbf{k}Ae^{-i(E/\hbar)t}e^{ikx})\}dV = A^2\hbar\mathbf{k}\int dV ;$$

but from making the ΣProb(x,t) = $\int\psi^*\psi dV$ = 1, we have $A^2\int dV = 1$, so

$$\mathbf{p}_{\text{free electron}} = \hbar\mathbf{k} .$$

This agrees with **DeBroglie's hypothesis** for a pure wave (that is, there exists a definite λ):

$$\mathbf{p} = h/\lambda = (h/2\pi)*(2\pi/\boldsymbol{\lambda}) = \hbar\mathbf{k} .$$

**For the electron in the periodic potential due to the ion cores**, we can express the spatial part of the wavefunction in terms of a Fourier series, so we have

$$\psi(x,t) = Ae^{-i(E/\hbar)t}\,{}_k\Sigma[C_k e^{ikx}] ,$$ or equivalently if we specify a particular $\mathbf{k}$:

$$\psi_k(\mathbf{r},t) = Ae^{-i(E/\hbar)t}\,{}_G\Sigma[C_{k+G}\,e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}]$$ (expressing $\psi_k$ as a Fourier series); therefore

$$\mathbf{p}_{el} = \int\{Ae^{i(E/\hbar)t}\,{}_G\Sigma[C_{k+G}^*\,e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}]\,(-i\hbar)Ae^{-i(E/\hbar)t}\,{}_G\Sigma[i(\mathbf{k}+\mathbf{G})C_{k+G}\,e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}]\}dV .$$

The cross terms of the multiplication of the sums will on average cancel out since we'll have to integrate an oscillating function of distance (the exponential). The only terms we need to consider then are the ones that give a cancellation of the exponential:

$$\mathbf{p}_{el} = \int\{A^2\,{}_G\Sigma[\hbar(\mathbf{k}+\mathbf{G})C_{k+G}^2]\}dV = \hbar\mathbf{k}\int\{A^2\Sigma C_{k+G}^2\}dV + \hbar\int\{A^2\Sigma\mathbf{G}C_{k+G}^2\}dV.$$

Since the ΣProb = 1 = $\int\{A^2\Sigma C_{k+G}^2\}dV$, we have

$$\mathbf{p}_{el} = \hbar\mathbf{k} + \hbar\int\{A^2\Sigma\mathbf{G}C_{k+G}^2\}dV = \mathbf{p}_{\text{free electron}} + \mathbf{p}_{\text{due to lattice}},$$

(where the **G** cannot be taken out of the Σ). **Thus the momentum of the electron in the periodic lattice is not the same as the momentum of the free electron.** This is due to the presence of the ion cores - that is, the difference in the momentum of the free electron to that of the electron in the material is due to the interaction of the electron with the ion cores in the material. This leads to the idea that we treat the electrons not as free electrons with the ordinary electronic mass, but as free electrons with an "effective" mass. We treat this next.