Notes for Lecture 2

Miller Indices, Quantum Mechanics

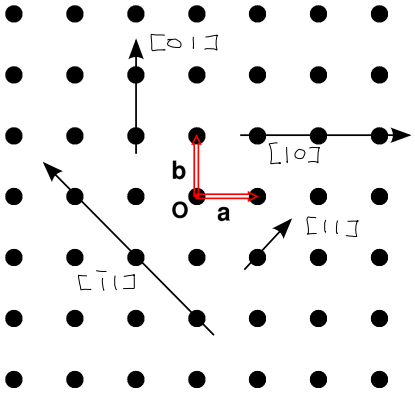
2.1 Directions

For a given crystal, there is a conventional notation for the direction.

Say, we have a basis and three (primitive translation) vectors $\vec{a}$, $\vec{b}$, and $\vec{c}$. Then, we have the following definition.

direction	meaning
$[lmn]$	parallel to $l\vec{a} + m\vec{b} + n\vec{c}$
$\langle lmn \rangle$	all directions physically equivalent to $[lmn]$

Here, l, m, n are integers. If any of it is negative, then the sign *goes on top of the magnitude*, not before it. This is the convention in the crystallography.



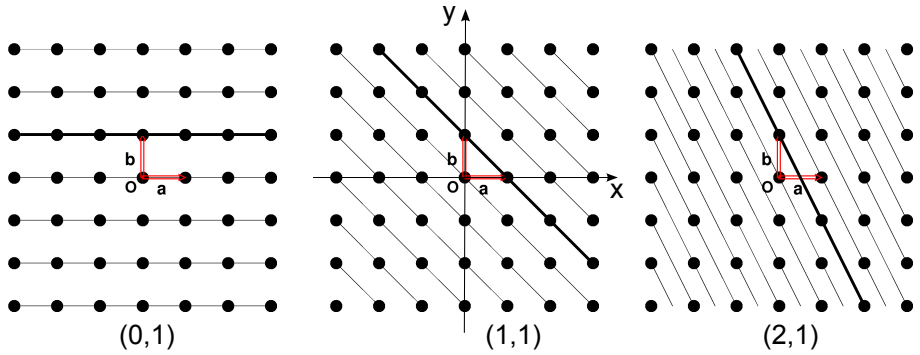
Consider the above figure. It is a 2D square lattice, where each filled circle is assumed to be a single kind of atom. Several directions are noted as arrows annotated with the $[lm]$ notation (two numbers suffice for a 2D lattice). One may ask "is the direction [11] and $[\bar{1}1]$ *physically* equivalent?" The answer is yes for this example. So, $\langle 11 \rangle$ means any of $[11], [\bar{1}1], [1\bar{1}], [\bar{1}\bar{1}]$ in this case.

2.2 Lattice Planes and Miller Indices

When a crystal is given, it means that we have a basis, which is something like a formula unit, and that basis is repeated indefinitely by three vectors $\vec{a}$, $\vec{b}$, and $\vec{c}$. Notice that this process can be thought of as forming a line first, by replicating the basis with the vector $l\vec{a}$, where l is an integer, and then forming a plane with by translating the line by $m\vec{b}$, where m is an integer, and, lastly, transforming the plane into the full three-dimensional crystal, by repeating the plane into $n\vec{c}$. It is obvious that it would make no difference if we change the order in which the three vectors $\vec{a}, \vec{b}, \vec{c}$ are used.

In this view, it can be seen easily that a three dimensional crystal is a collection of identical lattice/crystal planes (and each lattice plane is a collection of identical lattice lines).

It turns out that there are infinite ways to do this[1]. Namely, there are infinite ways to reduce a certain given crystal into a set of identical set of lattice planes. Let me illustrate this. For this illustration, though, I will take a two-dimensional crystal and divide it into lattice lines. This is because it is not convenient to visualize on a piece of paper how a three-dimensional crystal is divided into lattice planes. Nevertheless, the way that this reduction works is quite analogous.



[1]This is related to the fact that there are, actually, infinite ways to choose vectors $\vec{a}, \vec{b}, \vec{c}$ for a given crystal and a unit cell. Likewise, there are also infinite ways to choose a unit cell for a given crystal and the primitive lattice vectors $\vec{a}, \vec{b}, \vec{c}$

So, in the above figure, we consider a 2D square lattice again, but with the decomposition into lattice lines clearly marked in each panel. Below each panel is written indices. These are the so-called Miller indices.

The general procedure for obtaining Miller indices (in 3D) for a given set of lattice planes is the following.

1. Identify the lattice point corresponding to the origin (O) and $\vec{a}$, $\vec{b}$, and $\vec{c}$. Note that any lattice point can be defined as the origin.
2. Extend $\vec{a}$ to define the x axis, $\vec{b}$ to define the y axis, and $\vec{c}$ to define the z axis.
3. Identify and select a lattice plane which does not go through the origin, but closest to it. There will be always two such lattice planes. It is not important which one you select.
4. Find the intercepts x_i, y_i, z_i that this plane makes with the x, y, z axes, respectively. Here, x_i is in unit of $a = |\vec{a}|$, y_i is in unit of $b = |\vec{b}|$ and z_i is in unit of $c = |\vec{c}|$.
5. Invert these intercepts to get $\frac{1}{x_i}, \frac{1}{y_i}, \frac{1}{z_i}$.
6. If any of $\frac{1}{x_i}, \frac{1}{y_i}, \frac{1}{z_i}$ is a fraction, then multiply the least common denominator to each of these fractions to obtain three integers l, m, n. If all of $\frac{1}{x_i}, \frac{1}{y_i}, \frac{1}{z_i}$ are integers, then they define l, m, n.
7. (lmn) are the Miller indices for the given lattice planes.

This procedure is quite general, and applies even if $\vec{a}$, $\vec{b}$, $\vec{c}$ are not perpendicular to each other, or if their lengths differ. That is, this procedure applies to a general lattice, not just a cubic lattice.

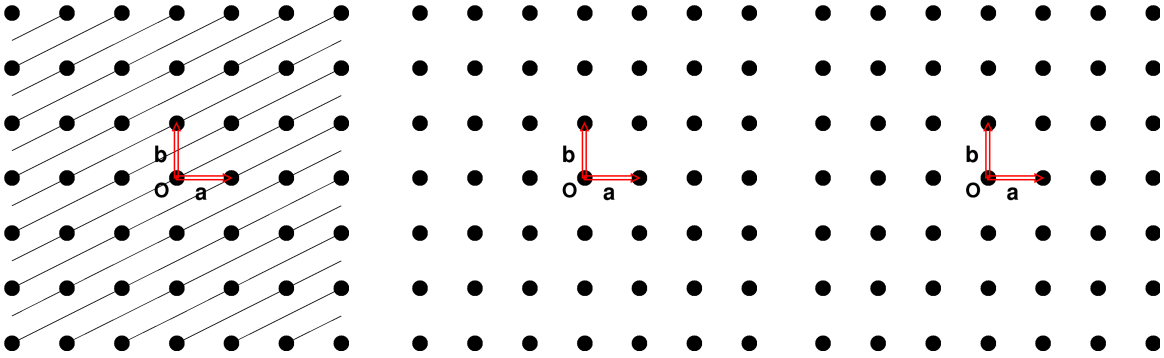
For the above 2D example figure, the lattice line identified in the 3rd step is marked with thick lines. It will be seen that the intercepts are $x_i = \infty, y_i = 1$ (left), $x_i = 1, y_i = 1$ (middle) and $x_i = 1/2, y_i = 1$ (right). Following steps 5-7, then Miller indices are $(0, 1)$, $(1, 1)$, and $(2, 1)$, as marked. Note that due to the ambiguity in step 3, these Miller indices could have been taken as $(0, \bar{1})$, $(\bar{1}, \bar{1})$, and $(\bar{2}, \bar{1})$, respectively. Namely, the overall sign of Miller indices can be positive or negative.

Here is a notation matter.

notation	meaning
(lmn)	lattice planes with Miller indices (lmn)
$\{lmn\}$	all Miller indices physically equivalent to (lmn)

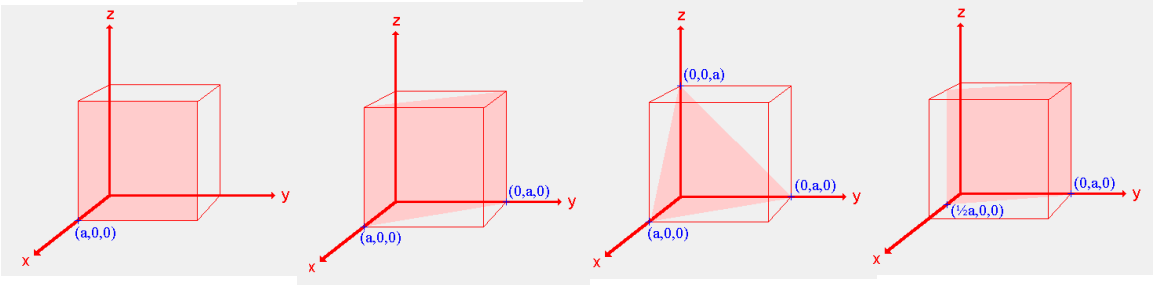
In the above square lattice example, $\{1,1\}$ would mean $(1,1)$ and $(\bar{1},1)$. Lattice lines $(1,1)$ and $(\bar{1},1)$ are distinct, but they are physically equivalent.

As an exercise, figure out the Miller indices of the lattice lines for the left diagram. In the middle diagram, indicate lattice lines with Miller indices $(\bar{1}1)$. In the right diagram, indicate lattice lines with Miller indices $(1,2)$.



Three dimensional cases are also straightforward. Here are some examples of the cubic lattice. These would be relevant in describing a Si crystal, for instance.

The Miller indices for these marked lattice planes are (100), (110), (111), and (210), respectively. The derivation is left for your exercise.



Images from http://www.chem.qmul.ac.uk/surfaces/scc/scat1_1b.htm

Finally, note that for a cubic lattice the surface normal of the lattice plane (lmn) points along the direction $[lmn]$. However, for other general lattices, this is not true.

2.3 Quantum Mechanics

A short summary of quantum mechanics is in order.

1. Any particle, when you get down to it, acts like a wave, in the sense that it satisfies a wave equation (e.g. Schrödinger equation). Qualitatively, this means

that the particle becomes "fuzzy," becomes a rather extended object, diffracts, "leaks" into barriers, and can tunnel through a barrier.

2. De Broglie "matter wave": $\lambda = h/p$. Or, $p = \hbar k$, where $\hbar = h/(2\pi)$.

3. Any wave (light or sound, for instance), when you get down to it, acts like a particle, in the sense that there is an indivisible quantum. The energy of the wave can increase or decrease in steps, discontinuously. Such a unit acts like a particle in scattering experiments, conserving momentum and energy. For momentum and energy, see above and below, respectively.

4. Photon = light quantum. The energy of a photon = $\hbar\omega = h\nu$. Here, $\nu = 1/T$ is the frequency (T = period), and $\omega = 2\pi\nu$ is the angular frequency[2]. Useful numbers to remember: $\hbar c$ = 1973 eV Å. 1 eV = 1.6e-19 Joules. $\hbar\omega$ (eV) = 12398 / λ (Å). Visible light: 4000 Å (purple) to 7000 Å (red), or 1.8 eV (red) to 3.1 eV (purple).

5. Particle = wave. Particle wave duality[3].

6. The uncertainty principle can be viewed as arising simply from the general property of a wave.
   Any wave, or any function, in real space ($\vec{r}$) can be described equivalently in the wave vector ($\vec{k}$) space. What do I mean by this? Obviously, you can describe a wave having some sort of a form in the real space, for example when you see a wave on the sea. But, did you know that *any* arbitrary function can be described as a sum over sine and cosine functions of different wave lengths, i.e. different wave vectors? Mathematically, this is called the Fourier theorem. It means that a real space function can be described equally well by specifying the distribution of wave vector components the function has. By "specifying" what I mean is assigning a number (a complex number to describe amplitude and phase) to each wave vector component, and thus it is precisely a process of defining a function in the wave vector ($\vec{k}$) space. Physically, you can think of a prism as an example Fourier transform device.
   If a single wave length, λ, describes a wave, then the wave is uniform in the real space. What do I mean by this? Consider a mono-chromatic wave in one dimension: the wave function is $\exp(i(kx - \omega t))$ up to a normalization constant. The magnitude of this wave function is uniform independent of x. Now, the fact that this wave is mono-chromatic means that it's got a single wave vector $k = 2\pi/\lambda$ only. The mathematical consequence of this is that the Fourier transform of this wave function, which is a function in the k space,

[2] If a physicist speaks of "frequency" without specifying which one, it is most likely ω, not ν! By the same token, "Planck constant" likely refers to $\hbar$ rather than h, when unspecified further.

[3] This fancy "duality" thing probably means that we are speaking a "wrong language," or that our everyday language is not good enough. The wave of ... what?

is zero everywhere except at the correct wave vector $2\pi/\lambda$. Another way of looking at it: what do you do when you need to form a wave packet with a certain localized distribution in the real space? – the answer is that you need to sum over waves of different wave vectors – and if you want to create a point-sharp wave function in real space, you would need to sum over waves with all wave vectors with equal weights! This duality – an extended (localized) wave function in $\vec{r}$ space corresponds to a localized (extended) wave function in $\vec{k}$ space – is the uncertainty principle: $\Delta x \Delta k \gtrsim 1$. Note that, in this view, there is no need to invoke the step of "measurement," which is an often-ill-defined and often-misunderstood term anyway. We could add that step in the usual way, if we wanted to, but we don't need to.
Through the De Broglie relation, $\Delta x \Delta k \gtrsim 1$ becomes $\Delta x \Delta p \gtrsim \hbar$, a more familiar form of the uncertainty principle.

7. A "classical particle" consists of extremely many quantum particles and they act quite "nicely" (i.e. according to Newton's laws, rather than Quantum Mechanics), since the quantum uncertainty is much smaller than the total quantity. For example, the size of a classical particle $L \gg \Delta L$, where ΔL is the quantum uncertainty. Also, the total energy $E \gg \Delta E$, where ΔE is the quantum energy uncertainty. And similarly for other quantities. A classical particle obeys Quantum Mechanics all the time. It is just that a new law, Newton's laws, emerges from the system when there are many many particles involved – and so as long as we are not breaking a classical particle very finely, we can forget about Quantum Mechanics, since the Newton's laws are "such an effective summarizing law" for many particles.

2.3.1 Hydrogen Atom

This is one of the most important examples in QM, and luckily it can be done without really going into QM.

We follow Bohr ("semi-classical picture"). This version of Bohr's quantum mechanics was a perplexing mixture of classical mechanics and quantum mechanics, at the time that Bohr proposed it. Its main advantage was that it explained atomic spectra data that were pouring out and were mysterious at the time. Bohr's theory was not really systematic – that had to wait other heroes of quantum mechanics – but his theory did act as a beacon to the systematic development of quantum mechanics.

Bohr's theory is a "fishy version" of quantum mechanics that we know today. However, this "fishy version" appeals to many people, as it is definitely closer to the sense of a large being like us, and even today this picture is invoked, when it can be,

on many occasions in research.

Consider an electron circling round a proton at a radius r, just as the Earth moves round the Sun. As the proton is ~ 2000 times heavier than an electron, it can be considered stationary. The centripetal force equation is given by

$$m\frac{v^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2}$$

Here, m is the electron mass ($mc^2 = 0.511$ MeV $= 0.511\times10^6$ eV), and ε_0 is the vacuum permittivity.

Bohr's inclusion of the "quantum effect" or the "wave effect" by hand is accomplished by the following:

$$mvr = n\hbar$$

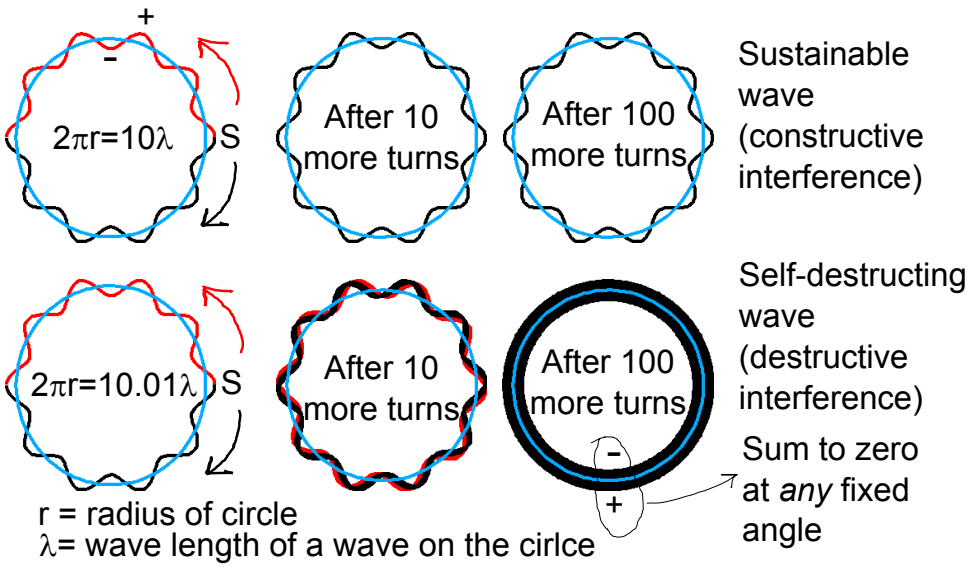
This is the so-called Bohr's "angular momentum quantization rule[4]." A more general form[5] is that $\oint m\vec{v}\cdot d\vec{r} = nh$ or $\oint L_z d\phi = nh$ ($\oint$ here means the integral over a closed classical path of motion), which goes by the name of **Bohr-Sommerfeld semi-classical quantization rule**. It is a very useful thing.

So, in some crude sense, it is as though only special values of r that satisfy the above two equations are selected. Namely, the radius of motion is quantized! This is a useful way to think about it, as long as one keeps in mind that in the more correct QM picture what is quantized is not the radius itself, but the expectation value of radius, such as $\langle r\rangle$ and $\langle 1/r\rangle$, etc. What Bohr got right by solving the above two equations is the quantization of $\langle 1/r\rangle$ and the quantization of energy.

The above Bohr-Sommerfeld quantization condition can be justified, if we start from QM and then take the classical limit. Instead of taking that path, here we will find the plausibility of this quantization condition by thinking like Bohr did, when the full QM did not exist. The following figure summarizes the point.

[4]This result is somewhat incorrect. In QM, the angular momentum is quantized, but differently.

[5]In this general form, the Bohr-Sommerfeld quantization condition is applicable for any bound state problem, not just a circular motion problem.



To understand this figure, imagine that the wave of an electron in a hydrogen atom is like a wave of a guitar string. Except that the guitar string is a circular string. Imagine that you pick one part of the string (S in the figure). When you do that, a wave propagates in two directions (the red direction and the black direction). The two diagrams on the left depict the situation when the two waves meet for the first time. In the upper row, we illustrate the situation when the circumference is exactly 10 times the wavelength. In the lower row, the circumference is 10.01 times the wavelength. There is a tiny difference in the two wavelengths, and in fact, when the red wave and the black wave meet for the first time, it is hard to notice that anything is really different. But, as the two waves turn and turn, the difference of the two situations clearly emerges. In the upper row situation, the red wave and the black wave are on top of each other and the value of the wave for any angle is always one value – i.e. the red wave and the black wave always interfere constructively. In the lower row situation, both the red wave and the black wave fill a finite area after sufficient number of turns (the plot of the red wave is right underneath the plot of the black wave, and is thus invisible in this figure). For any angle, then, there is an equal number of positive amplitudes (radius greater than the circle) and an equal number of negative amplitudes (radius smaller than the circle) – so this wave is not sustainable – it self-destructs.

The condition for this wave to exist

$$2\pi r = n\lambda$$

becomes the above angular momentum quantization rule $mvr = n\hbar$ if we use the De Broglie relation $\lambda = h/(mv)$.

From the centripetal force equation and this Bohr-Sommerfeld quantization condition, the following result is easily derived:

$$E_n = -\frac{R}{n^2}$$

$$\frac{1}{r_n} = \frac{1}{a_B}\frac{1}{n^2}$$

$R = 13.6$ eV (Rydberg constant). $a_B = 0.529$ Å (Bohr radius). $n = 1, 2, 3, \cdots$. E_n is the quantized energy levels. r_n is the "quantized radius" (see comment near the end of page 7).