

Quanta and Wave Particle duality

We have only looked at interference, diffraction and polarisation effects until now. These are all effects of the wave description of light. However, when we look at interactions of light with matter: absorption, emission and scattering, we find very different behaviour than what we expect for waves.

The behaviour is better understood if we think of light as particle-like packets of energy, called photons or light quanta. We also find that the internal energy of atoms can only exist in discrete levels, the energy is quantised.

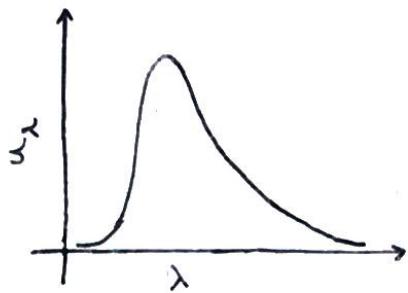
Moreover, what we previously considered as particles, like electrons, can exhibit wave-like behaviour. So light can act like a particle and particles can act like waves. This double-nature is called wave-particle duality and confused physicists for a long time!

Line Spectra

We have already seen that a prism or a diffraction grating can be used to split light into its components. If you examine the light from an electric discharge tube, like a neon sign, or from salt heated in a flame, the light has a spectrum of discrete frequencies. Each element has a characteristic pattern of these "spectral lines" that depends on its internal atomic structure.

Blackbody Radiation

A blackbody is an ideal absorber and emitter of radiation. Experimental data for the Sun is shown:



As can be seen, there is a clear peak in a certain band of wavelength. This is the range 400 - 700 nm, the visible band of light. This is why our eyes evolved to be sensitive to this band.

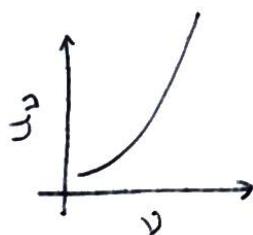
But what is u_λ on the y-axis? u_λ is the energy density of thermal radiation in wavelength, i.e $u_\lambda d\lambda$ is the energy divided by volume for radiation with wavelength in the range $[\lambda, \lambda + d\lambda]$. We can also define the energy density in frequency ν as u_ν .

Classical Physics could not explain the measured u_ν or the equivalent u_λ . The classical result produced the equation

$$u_\nu = \frac{8\pi k T \nu^2}{c^3}$$

This is the Rayleigh-Jeans Law.

A big problem with this is when integrating over all frequencies. ν is divergent and so gives an infinite total energy per unit volume. It would give the shape:



As we saw above, this is not what the experimental data shows. The classical physics shape would give infinite total energy per unit volume! This was called the ultraviolet catastrophe.

To resolve the UV catastrophe, Planck proposed that the energy of light at each frequency f , comes in quanta of size $h\nu$.

$$E = h\nu = \frac{h}{\lambda}$$

Energy is quantised! This is one of the most important statements in the history of science.

h is Planck's constant: $h = 6.63 \times 10^{-34} \text{ Js}$

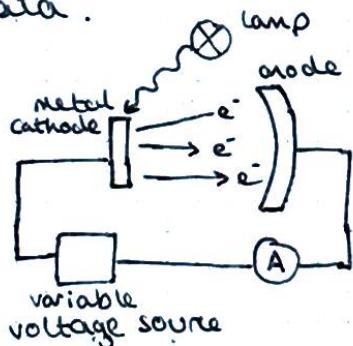
The relative probability of exciting a quantum (called the Boltzmann weight) is then:

$$\text{Boltzmann weight} = e^{-h\nu/kT}$$

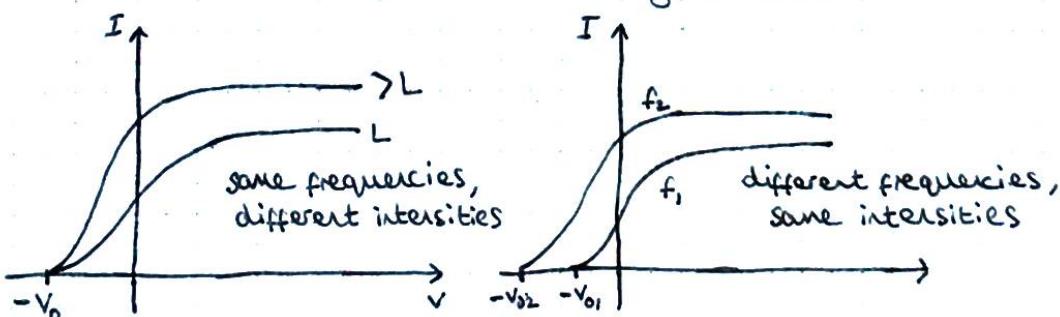
This "cuts off" the energy at higher frequencies, resolving the UV catastrophe.

Photoelectric Effect

EM radiation incident on a metal can cause it to eject electrons. From experiments on similar apparatus to below, it was clear that classical EM radiation could not explain data.



When a voltage is applied and the lamp is shone on the metal. By varying the intensity of the lamp and the voltage of the source, different Current-Voltage graphs can be generated:



The noticed effects of varying voltage and intensity were:

- 1) As V increases at fixed Intensity and frequency, eventually all the electrons are swept up and a maximum current is reached. This is the saturation current.
- 2) If V is made negative, eventually all the electrons can be stopped from reaching the anode and the current is 0.
- 3) The negative voltage that the current is switched off at, V_0 , is called the stopping potential and is the same for all intensities. It changes for different frequencies, becoming more negative for higher frequencies.
- 4) There is a minimum frequency f_0 called the threshold frequency below which there is no photocurrent.
- 5) If the intensity is increased at fixed frequency, the saturation increases proportional to the intensity increase.
- 6) There is no threshold intensity. Provided $f > f_0$, for ever very low intensities, a current is produced immediately.

Classical EM radiation would produce different IV curves than the ones observed, i.e a high intensity low frequency ($f < f_0$) should still cause a current. At low intensity we also expect it to take some time before the electron has gained enough energy to be emitted. But the current is observed immediately.

So what was Einstein's explanation for all of this?

Einstein explained the photoelectric effect data by assuming that EM radiation comes in discrete packets of energy $E = hf$.

Consider the effect of a negative voltage on the system. At the stopping voltage V_0 , no electrons reach the anode. If the electrons need kinetic energy to get to the anode, we have to do work to stop them. Thus, the maximum kinetic energy of the electrons is given by:

$$K_{\max} = eV_0 \quad \text{where } e \text{ is the charge of the electron}$$

and V_0 is the stopping voltage.

To escape the metal, the electrons must overcome the attraction of the positive ions. So there is a minimum energy, called the work function ϕ , that the electron must have. This is the energy it uses to break free.

By conservation of energy:

$$K_{\max} = eV_0 = hf - \phi$$

If the frequency is too low, the electron will not have enough energy, hence the threshold frequency.

$$\phi = h\nu_0$$

This is the equation for the work function

Photon Momentum

We know from relativity that $E^2 = p^2c^2 + m^2c^4$. Since photons are massless we get $E = pc$. So the momentum of a photon is given by:

$$p = \frac{E}{c} = \frac{hf}{c} = \frac{h}{\lambda}$$

X-ray Scattering and Compton Scattering -

When X-rays scatter from matter, they sometimes emerge with a lower frequency. This makes absolutely no sense according to classical physics! It would be like blue light being reflected and coming out blue! The process is now known as Compton Scattering.

The process can again be explained by photons. If a photon collides with, say, an electron and the electron recoils, then the electron has gained kinetic energy. This means the photon must lose energy and, since $E = hf$, the frequency must fall. So how much does it fall?

Consider a photon with energy $E_0 = hf_0$, momentum p_0 and wavelength λ_0 , colliding with a stationary electron m . After the collision the photon has energy E , momentum p and wavelength λ . The electron has energy E_e and momentum p_e . θ is the angle the photon is scattered at.

$$\text{Using conservation of Energy: } E_0 + mc^2 = E + E_e \quad ①$$

$$\text{Using conservation of Momentum: } p_0 = p + p_e \quad ②$$

$$\text{From ①: } E_e = E_0 - E + mc^2 = p_0 c - pc + mc^2$$

$$\text{From ②: } p_e = p_0 - p \Rightarrow p_e^2 = (p_0 - p)^2 = p_0^2 - 2p_0 \cdot p + p^2 \\ = p_0^2 - 2p_0 p \cos\theta + p^2$$

Now we can use the energy-momentum relation $E_e^2 = p_e^2 c^2 + m^2 c^4$

$$E_e = p_0 c - pc + mc^2$$

$$p_e^2 = p_0^2 - 2p_0 p \cos\theta + p^2$$

} substitute into $E_e^2 = p_e^2 c^2 + m^2 c^4$

$$(p_0 c - pc + mc^2)^2 = (p_0^2 - 2p_0 p \cos\theta + p^2) c^2 + m^2 c^4$$

$$p_0^2 c^2 - 2p_0 p c^2 + 2p_0 m c^3 + p^2 c^2 - 2p_0 m c^3 + m^2 c^4 = p_0^2 c^2 - 2p_0 p \cos\theta c^2 + p^2 c^2 + m^2 c^4$$

$$- 2p_0 p c^2 + 2p_0 m c^3 - 2p_0 m c^3 = - 2p_0 p \cos\theta c^2$$

$$2mc^2(p_0 c - pc) = 2p_0 p c^2(1 - \cos\theta)$$

Now divide by $2p_0 c^2$:

$$\frac{mc}{p} - \frac{mc}{p_0} = 1 - \cos\theta \Rightarrow \frac{1}{p} - \frac{1}{p_0} = \frac{1}{mc}(1 - \cos\theta)$$

using $p = \frac{\hbar}{\lambda}$, we get:

$$\frac{\lambda}{n} - \frac{\lambda_0}{n} = \frac{1}{mc}(1 - \cos\theta)$$

$$\therefore \boxed{\lambda - \lambda_0 = \frac{\hbar}{mc}(1 - \cos\theta)}$$

This is Compton's relation
for the wavelength shift

The maximum shift in wavelength occurs when $\theta = 90^\circ$
so that $\cos\theta = -1$

$$\boxed{(\lambda - \lambda_0)_{\max} = \Delta\lambda_{\max} = \frac{2\hbar}{mc}}$$

Matter Waves

In the same way that we can consider light as photons, we can define a wavelength for a massive particle of momentum, p . This is called the de Broglie wavelength:

Remember:
 $p = \gamma m v$

$$\lambda = \frac{h}{p} = \frac{h}{\gamma m v}$$

where $\gamma = \frac{1}{\sqrt{1 - v^2/c^2}}$
and $\gamma = 1$ for non-relativistic velocities

We can also define a frequency for the wave, which like for a photon depends on the energy of the particle

In a non-relativistic case, the energy of the particle is the sum of its kinetic energy and its rest mass:

$$E = \frac{1}{2} m v^2 + m c^2 = \frac{m^2 v^2}{2m} + m c^2 \quad \text{so:}$$

for a non-relativistic case:

$$E = \frac{p^2}{2m} + m c^2$$

In a relativistic case, we can use the relation $E^2 = p^2 c^2 + m^2 c^4$

for a relativistic case

$$E = \sqrt{p^2 c^2 + m^2 c^4}$$

But why are we modelling matter like waves at all?
When does it behave like that?

Electrons are very weird...

Electron Diffraction

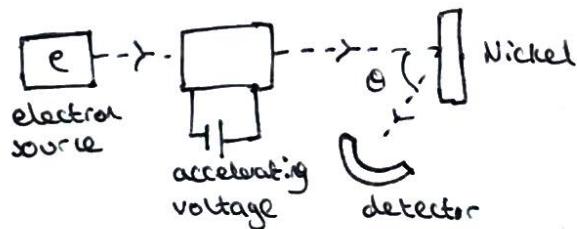
In a famous experiment in 1927 by Davisson and Germer, electrons were scattered off a nickel surface. The pair had accidentally created large single-crystal domains of width comparable to the electron beam. They had done this by trying to remove the oxidation from the Nickel by baking it.

The electrons were given a kinetic energy by being accelerated through a potential difference:

$$K = eV = \frac{p^2}{2m} \Rightarrow p = \sqrt{2meV}$$

This gives a de Broglie wavelength $\lambda = \frac{h}{\sqrt{2meV}}$

The pair found peak intensities of scattered electrons at certain angles θ between the incident beam and the line from the Nickel to the detector:



The condition for peaks is given by the Bragg condition. Usually, this is $2dsin\theta = m\lambda$ but since the beam is incident perpendicular to the plane, there is only one "triangle" so the condition is:

$$dsin\theta = m\lambda = \frac{mh}{\sqrt{2meV}}$$

This is what the experiment found!

Single and Double Slit Experiments with Electrons

Recall that with single-slit diffraction of light, we saw something like . So what do we see with electrons?

We start by sending electrons through the slit in a beam. The electrons hit a screen after being diffracted. The screen is covered in a scintillating material that causes the spot of collision to glow. You observe that the glowing spots seem to appear in random places but if you keep recording the positions and then plot them, you see a pattern:



This is what you expect for classical diffraction intensity patterns but the way it appeared is quite weird. The individual electrons didn't follow the same path, even though they were treated identically.

The intensity pattern tells you the relative probability of an electron hitting that point. The de Broglie wavelength is describing a probability wave!

This same thing can be done with double slits and we get the same result. Apparently random flashes that when plotted give the same intensity curve as light.

So the function that describes the electron is a probability density function! But what is that function?

Quantum Wavefunctions

A wave function describing light waves is the electric field $E(\xi, t)$. The energy density for this is given by $\epsilon_0 |E|^2$. So:

$$\text{The energy in a volume } dV = \underline{\epsilon_0 |E|^2 dV}$$

For light of frequency f , the individual photons have energy hf .
So:

$$\text{The number of photons in } dV = \frac{\epsilon_0 |E|^2}{hf} dV \propto |E|^2 dV$$

taking $\frac{\epsilon_0}{hf}$ to be a constant.

Now, as we make dV smaller and smaller, there will eventually be less than one photon in the volume. However, the number of photons can only be discrete, non-negative integers. So we instead say that the number of photons is proportional to the average number counted. i.e. When you measure, you measure only integers but the average need not be an integer. This is a probability interpretation.

Now let's do this for our proposed wavefunction for electrons $\Psi(\xi, t)$.

$$\text{The average number of electrons in } dV \propto |\Psi(\xi, t)|^2 dV$$

So what is $|\Psi|^2$? Since we are working with quantum mechanics, we have to take Ψ to be a complex quantity. Recall that for a complex number z , $|z|^2 = z\bar{z}$.

$$\text{So: } \Psi(\underline{r}, t) = \text{Re } \Psi(\underline{r}, t) + \text{Im } \Psi(\underline{r}, t)$$

$$\underline{|\Psi|^2} = (\text{Re } \Psi)^2 + (\text{Im } \Psi)^2$$

Thinking back to the single slit experiment, we shouldn't say that it is the average number of electrons that is proportional to $\int |\Psi|^2 dV$. Instead, we say that it is the probability of finding an electron in a volume.

$$P(\text{finding an electron in a volume } dV \text{ at } \underline{r}, t) \propto |\Psi(\underline{r}, t)|^2 dV$$

Since it is a probability function, we normalise it:

$$\int_{-\infty}^{\infty} |\Psi(\underline{r}, t)|^2 dV = 1 \quad \text{This makes it a true probability function.}$$

So what does this mean?

- Quantum Mechanics will provide you with a wave equation called the Schrödinger equation that lets you determine $\Psi(\underline{r}, t)$
- This lets you compute the probability of an electron in a given volume at a given time.
- You cannot predict the exact path an electron will take as you can in classical physics.
- You can give precise probabilities for the results of detecting electrons in various positions.

If you know $\Psi(\underline{r}, t)$ you know everything about the electron!

The Uncertainty Principle

Consider single slit diffraction of electrons. Individual electrons will end up in lots of places, with 85% of them being in a central maximum. The maxima are given by $\sin\theta = \frac{m\lambda}{a}$. Assuming the angle between the first central maxima and its neighbour is small, the central maxima extends out

$$\Theta_1 = \frac{\lambda}{a} \text{ where } a \text{ is the slit width.}$$

To travel at this angle, the electron's momentum components must be related by $\tan\Theta_1 = \frac{p_y}{p_x} \approx \underline{\Theta_1 = \frac{p_y}{p_x}}$

$$\text{so: } \frac{p_y}{p_x} = \frac{\lambda}{a} \Rightarrow \underline{p_y = p_x \frac{\lambda}{a}}$$

This allows for the electrons to hit the central maximum, but the electrons will hit the centre over a range of y :

$$-p_x \frac{\lambda}{a} \leq p_y \leq p_x \frac{\lambda}{a} \quad \text{This is the uncertainty in } p_y.$$

Since some electrons are outside the central maximum, the uncertainty in p_y , Δp_y , can be said to be:

$$\Delta p_y \geq p_x \frac{\lambda}{a} \text{ but } \lambda = \frac{h}{p} \approx \frac{h}{p_x} \text{ so: } \underline{\Delta p_y \geq \frac{h}{a}}$$

a is the width of the slit which can be used as a measure of the uncertainty in the electrons' y -positions.

$$\therefore \boxed{\Delta y \Delta p_y \geq h}$$

This is a very rough form of Heisenberg's Uncertainty Principle.

If we make the slit narrower, it makes the diffraction pattern wider. We can see this in the uncertainty principle.

Wave Packets

Consider a wavefunction of a single sinusoidal plane wave in 1D: $\Psi(x, t) = Ae^{-ikx - wt}$

From the de Broglie wavelength, we can work out the momentum:

$$p = \frac{h}{\lambda} = \frac{h}{2\pi/k} = \frac{h}{2\pi} k = \underline{\underline{tk}} \quad \text{where } t = \frac{h}{2\pi}$$

Since we know the wave number, k , we definitely know the momentum precisely. However, we can see that $|\Psi|^2 = |A|^2$ so the probability distribution is uniform.

This tells us that there is equal probability of the particle being at any x ! We know the momentum so we can't know the position! This is one extreme of the uncertainty principle.

Can we construct wavefunctions where the probability to find the particle is concentrated around a value for x ? On the other extreme, we could know the exact position but have completely unknown momentum!

We can do this by summing together plane waves with different momenta or wavelengths but a particular x . This works with Fourier Series to give:

This is called coordinate space wavefunction.

$$\Psi(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} A(k) e^{ikx} dk$$

By choosing $A(k)$, we can make any shape we like for $\Psi(x)$.

This is called momentum space wavefunction

$$A(k) = \int_{-\infty}^{\infty} \Psi(x) e^{-ikx} dx$$

Conversely, we can find $A(k)$ for any given Ψ .

Gaussian Wavepackets

Consider the coordinate space function of the form:

$$\Psi(x) = Ne^{ik_0x - x^2/4\sigma^2} \quad \text{where } N \text{ is a normalisation factor}$$

The probability density in x is given by $|\Psi|^2 = \Psi \cdot \Psi^*$

$$|\Psi(x)|^2 = |N|^2 e^{-x^2/2\sigma^2}$$

This is in the form of a Gaussian function with standard deviation σ . The wavepacket is localised around $x=0$ (the centre of this gaussian). The wave number in Ψ is k_0 so the momentum is $p_0 = \hbar k_0$.

The wavefunction in the momentum space is given by:

$$A(k) = \int_{-\infty}^{\infty} \Psi(x) e^{-ikx} dx = N \int_{-\infty}^{\infty} e^{ik_0x - x^2/4\sigma^2} e^{-ikx} dx$$
$$A(k) = N' e^{-i(k-k_0)^2 \sigma^2}$$

The probability density in k is given by:

$$|A(k)|^2 = |N'|^2 e^{-2(k-k_0)^2 \sigma^2}$$

For this to be a normal function, there needs to be an exponent in the form $\frac{1}{2\sigma_k^2}$ where σ_k is the standard deviation of a gaussian in k .

$$\therefore 2\sigma^2 = \frac{1}{2\sigma_k^2} \Rightarrow \sigma_k = \frac{1}{2\sigma}$$

So the standard deviation of the momentum-space gaussian is $\frac{1}{2\sigma}$, where σ is the standard deviation of the coordinate space.

In quantum mechanics, the uncertainty of a state is defined to be the standard deviation of probability distribution:

$$\Delta x = \text{std}(|\Psi(x)|^2) = \sigma$$

$$\Delta k = \text{std}(|A(k)|^2) = \sigma_k = \frac{1}{2\sigma}$$

Since $p = \hbar k$, $\Delta p = \hbar \Delta k = \hbar \sigma_k = \frac{\hbar}{2\sigma}$

This gives $\Delta x \Delta p = \sigma \frac{\hbar}{2\sigma} \Rightarrow \boxed{\Delta x \Delta p = \frac{\hbar}{2}}$

for any wavefunction, it can be shown that:

$$\boxed{\Delta x \Delta p \geq \frac{\hbar}{2}}$$

which is the precise form of the Heisenberg uncertainty relation.

The Gaussian wavepackets are an example of minimum uncertainty.

Zero-point Energy of Harmonic Oscillator

As a consequence of the uncertainty principle, you cannot confine a particle to a small region at rest. As you confine it more closely, you decrease Δx its position uncertainty, but increase Δp its momentum uncertainty. This means the particle "jiggles" more and more.

Consider a particle confined to a small region of width $a = \Delta x$. This gives a momentum uncertainty of $\Delta p \geq \frac{\hbar}{2a}$. We can then find an expression for the kinetic energy.

So an estimate for the particle's kinetic energy is

$$K = \frac{P^2}{2M} \approx \frac{(\Delta P)^2}{2M} = \frac{\hbar^2}{8Ma^2}$$

We say that the particle has a minimum energy of roughly $\frac{\hbar^2}{Ma^2}$. Applying this to a harmonic oscillator, we state the kinetic and potential energies:

$$T = \frac{(\Delta P)^2}{2M} \quad V = \frac{1}{2} M \omega^2 (\Delta x)^2$$

where ω is the classical angular frequency of the oscillator.

for a quantum mechanical oscillator, the lowest energy state (ground state) is at small $|\Delta x|$. But by the argument earlier, more localised x (smaller Δx) means larger momentum uncertainty (and hence larger kinetic energy).

So we need to find the tradeoff between increasing localisation and increasing momentum uncertainty to find the lowest total energy. The lowest total energy will be non-zero.

$$\begin{aligned} \text{Total Energy } E &= T + V = \frac{(\Delta P)^2}{2M} + \frac{1}{2} M \omega (\Delta x)^2 \\ &= \frac{\hbar^2}{8M(\Delta x)^2} + \frac{1}{2} M \omega (\Delta x)^2 \end{aligned}$$

minimising E with respect to Δx leads to:

$$E_{\min} = \frac{\hbar \omega}{2}$$

This energy is sometimes called the zero-point energy.

Atomic Energy Levels

Gases absorb light at wavelengths that are characteristic of the atoms forming the gas. They also emit light at these same wavelengths. This absorption/emission at fixed frequencies implies that the atoms radiate/absorb photons with discrete Energies $E = hf$. This is explained if the total energy of an atom is quantised so that when the atom jumps from energy states E_i to E_j with $E_i > E_j$, it radiates a photon of energy $E = E_i - E_j = hf$.

When a photon of energy $E_i - E_j$ strikes an atom, it can jump from energy state E_j to E_i when $E_i > E_j$.

In 1885, Balmer found an empirical formula:

$$\frac{1}{\lambda} = R \left(\frac{1}{n'^2} - \frac{1}{n^2} \right)$$

where n' and n are the integers corresponding to energy states and R is the Rydberg constant.

Multiplying by hc , we get $\frac{hc}{\lambda} = hcR \left(\frac{1}{n'^2} - \frac{1}{n^2} \right)$

Since $\frac{hc}{\lambda} = hf$, we interpret this as the energy of the photon, which is the difference in energy between the energy states.

$$E_n - E_{n'} = hcR \left(\frac{1}{n'^2} - \frac{1}{n^2} \right)$$

This works for n and n' up to a constant, which we set to 0, giving us:

$$E_n = -\frac{hcR}{n^2} \quad \text{for } n \geq 1$$

Classical Difficulties with the Hydrogen Atom

There are two problems with the classical description of an atom as a nucleus (comprising nearly all the mass but almost none of the volume) and a cloud of orbiting electrons. The problems are:

Stability problem - The classical picture says the electron is orbiting the nucleus. This means it is continuously accelerating. Classical EM states that it must therefore radiate. However, any radiated energy would cause the orbit to decay and the electron to spiral into the nucleus, destabilising it.

Identity problem - If the orbits are somehow stable, there would be a continuous spectrum of allowed energies since the orbit can take any radius. But we only observe discrete energies in radiation.

Boltz proposed quantisation of Angular Momentum, L .

Only orbits for which angular momentum is a multiple of \hbar are allowed.

$$L = pr = n\hbar$$

This means only certain orbital radii are allowed, answering the identity problem. However, this doesn't answer everything and doesn't work with atoms that have more than one electron.

So what is the answer? You'll find out next year!