2

Introduction to Quantum Physics

The gestation of Quantum Physics has been very long and its phenomenological foundations were various. Historically the original idea came from the analysis of the black body spectrum. This is not surprising since the black body, in fact an oven in thermal equilibrium with the electromagnetic radiation, is a simple and fundamental system once the law of electrodynamics are established. As a matter of fact many properties of the spectrum can be deduced starting from the general laws of electrodynamics and thermodynamics; the crisis came from the violation of energy equipartition. This suggested to Planck the idea of *quantum*, from which everything originated. Of course a long sequence of different phenomenological evidences, first of all the photoelectric effect, the line nature of atomic spectra, the Compton effect and so on, gave a compelling evidence for the new theory.

Due to the particular limits of the present notes an exhaustive analysis of the whole phenomenology is impossible. Even a clear discussion of the black body problem needs an exceeding amount of space. Therefore we have chosen a particular line, putting major emphasis on the photoelectric effect and on the inadequacy of a classical approach based on Thomson's model of the atom, followed by Bohr's analysis of the quantized structure of Rutherford's atom and by the construction of Schrödinger's theory. This does not mean that we have completely overlooked the remaining phenomenology; we have just presented it in the light of the established quantum theory. Thus, for example, Chapter 3 ends with the analysis of the black body spectrum in the light of quantum theory.

2.1 The Photoelectric Effect

The photoelectric effect was discovered by H. Hertz in 1887. As sketched in Fig. 2.1, two electrodes are placed in a vacuum cell; one of them (C) is hit by monochromatic light of variable frequency, while the second (A) is set to a negative potential with respect to the first, as determined by a generator G and measured by a voltmeter V.

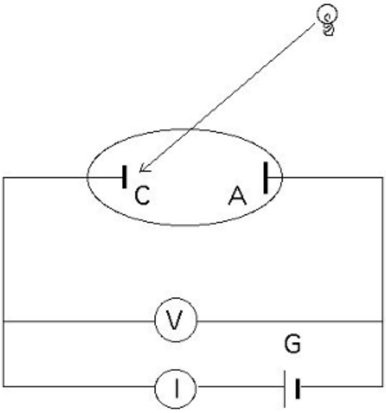


Fig. 2.1. A sketch of Hertz's photoelectric effect apparatus

By measuring the electric current going through the amperometer I, one observes that, if the light frequency is higher than a given threshold ν_V, determined by the potential difference V between the two electrodes, the amperometer reveals a flux of current i going from A to C which is proportional to the flux of luminous energy hitting C. The threshold ν_V is a linear function of the potential difference V

$$\nu_V = a + bV \ . \tag{2.1}$$

The reaction time of the apparatus to light is substantially determined by the (RC) time constant of the circuit and can be reduced down to values of the order of 10^{-8} s. The theoretical interpretation of this phenomenon remained an open issue for about 14 years because of the following reasons.

The current direction and the possibility to stop it by increasing the potential difference clearly show that the electric flux is made up of electrons pulled out from the atoms of electrode C by the luminous radiation.

A reasonable model for this process, which was inspired by Thomson's atomic model, assumed that electrons, which are particles of mass $m = 9\ 10^{-31}$ Kg and electric charge $-e \simeq -1.6\ 10^{-19}$ C, were elastically bound to atoms of size $R_A \sim 3\ 10^{-10}$ m and subject to a viscous force of constant η. The value of η is determined as a function of the atomic relaxation time, $\tau = 2m/\eta$, that is the time needed by the atom to release its energy through radiation or collisions, which is of the order of $\tau = 10^{-8}$ s. Let us confine ourselves to considering the problem in one dimension and write the equation of motion for an electron

$$m\ddot{x} = -kx - \eta\dot{x} - eE\,, \tag{2.2}$$

where E is an applied electric field and k is determined on the basis of atomic frequencies. In particular we suppose the presence of many atoms with different frequencies continuously distributed around

$$\sqrt{\frac{k}{m}} = \omega_0 = 2\pi\nu_0 \sim 10^{15}\ \mathrm{s}^{-1}\,. \tag{2.3}$$

If we assume an oscillating electric field $E = E_0\cos(\omega t)$ with $\omega \sim 10^{15}\ \mathrm{s}^{-1}$, corresponding to visible light, then a general solution to (2.2) is given by

$$x = x_0\cos(\omega t + \phi) + A_1 e^{-\alpha_1 t} + A_2 e^{-\alpha_2 t}\,, \tag{2.4}$$

where the second and third term satisfy the homogeneous equation associated with (2.2), so that $\alpha_{1/2}$ are the solutions of the following equation

$$m\alpha^2 - \eta\alpha + k = 0\,,$$

$$\alpha = \frac{\eta \pm \sqrt{\eta^2 - 4km}}{2m} = \frac{1}{\tau} \pm \sqrt{\frac{1}{\tau^2} - \omega_0^2} \simeq \frac{1}{\tau} \pm \mathrm{i}\,\omega_0\ , \tag{2.5}$$

where last approximation is due to the assumption $\tau \gg \omega_0^{-1}$.

Regarding the particular solution $x_0\cos(\omega t+\phi)$, we obtain by substitution:

$$-m\omega^2 x_0\cos(\omega t+\phi) = -kx_0\cos(\omega t+\phi) + \eta\omega x_0\sin(\omega t+\phi) - eE_0\cos(\omega t) \tag{2.6}$$

hence

$$\begin{aligned}(k - m\omega^2)x_0\,(\cos(\omega t)cos\phi - \sin(\omega t)\sin\phi)\\ = \eta\omega x_0\,(\sin(\omega t)cos\phi + \cos(\omega t)\sin\phi) - eE_0\cos(\omega t)\end{aligned}$$

from which, by taking alternatively $\omega t = 0, \pi/2$, we obtain the following system

$$\begin{aligned}\left(m\left(\omega_0^2 - \omega^2\right)\cos\phi - \eta\omega\sin\phi\right)x_0 &= -eE_0\,,\\ m\left(\omega_0^2 - \omega^2\right)x_0\sin\phi + \eta\omega\ x_0\cos\phi &= 0\end{aligned} \tag{2.7}$$

which can be solved for ϕ

$$\tan\phi = \frac{2\omega}{\tau\left(\omega^2 - \omega_0^2\right)}\,,$$

$$\cos\phi = \frac{\omega^2 - \omega_0^2}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + \frac{4\omega^2}{\tau^2}}}\,, \qquad \sin\phi = \frac{(2\omega/\tau)}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + \frac{4\omega^2}{\tau^2}}} \tag{2.8}$$

and finally for x_0, for which we obtain the well known resonant form

$$x_0 = \frac{eE_0/m}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + \frac{4\omega^2}{\tau^2}}} \,. \tag{2.9}$$

To complete our computation we must determine A_1 and A_2. On the other hand, taking into account (2.5) and the fact that x is real, we can rewrite the general solution in the following equivalent form:

$$x = x_0 \cos(\omega t + \phi) + A\mathrm{e}^{-t/\tau} \cos(\omega_0 t + \phi_0) \,. \tag{2.10}$$

If we assume that the electron be initially at rest, we can determine A and ϕ_0 by taking $x = \dot{x} = 0$ for $t = 0$, i.e.

$$x_0 \cos\phi + A\cos\phi_0 = 0 \,, \tag{2.11}$$

$$x_0 \; \omega \sin\phi = -A\left(\frac{\cos\phi_0}{\tau} + \omega_0 \sin\phi_0\right) \,, \tag{2.12}$$

hence in particular

$$\tan\phi_0 = \frac{\omega}{\omega_0}\tan\phi - \frac{1}{\omega_0\tau} \,. \tag{2.13}$$

These equations give us enough information to discuss the photoelectric effect without explicitly substituting A in (2.10).

Indeed in our simplified model the effect, i.e. the liberation of the electron from the atomic bond, happens as the amplitude of the electron displacement x is greater than the atomic radius. In equation (2.10) x is the sum of two parts, the first corresponding to stationary oscillations, the second to a transient decaying with time constant τ. In principle, the maximum amplitude could take place during the transient or later: to decide which is the case we must compare the value of A with that of x_0. It is apparent from (2.11) that the magnitude of A is of the same order as x_0 unless $\cos\phi_0$ is much less than $\cos\phi$. On the other hand, equation (2.13) tells us that, if $\tan\phi_0$ is large, then $\tan\phi$ is large as well, since $(\omega_0\tau)^{-1} \sim 10^{-7}$ and $\omega/\omega_0 \sim 1$. Therefore, the order of magnitude of the maximum displacement is given by x_0, and can be sensitive to the electric field frequency. That happens in the resonant regime, where ω differs from ω_0 by less than $2\sqrt{\omega/\tau}$.

Let us consider separately the generic case from the resonant one. In the first case the displacement is of the order of $eE_0/(\omega^2 m)$, since the square root of the denominator in (2.9) has the same order of magnitude as ω^2. In order to induce the photoelectric effect it is therefore necessary that

$$\frac{eE_0}{\omega^2 m} \sim R_A \,,$$

from which we can compute the power density needed for the luminous beam which hits electrode C:

$$P = c\epsilon_0 E_0^2 \sim c\epsilon_0 \left(\frac{R_A \omega^2 m}{e}\right)^2 \,,$$

where c is the speed of light and ϵ_0 is the vacuum dielectric constant. P comes out to be of the order of 10^{15} W/m^2, a power density which is difficult to realize in practice and which would anyway be enough to vaporize any kind of electrode. We must conclude that our model cannot explain the photoelectric effect if ω is far from resonance. Let us consider therefore the resonance case and set $\omega = \omega_0$. On the basis of (2.11), (2.13) and (2.9), that implies:

$$\phi = \phi_0 = \frac{\pi}{2} \, , \quad A = -x_0 \, ,$$

hence

$$x = \frac{-eE_0\tau}{2m\omega_0}\left(1 - \mathrm{e}^{-t/\tau}\right)\sin(\omega_0 t) \, . \tag{2.14}$$

In order for the photoelectric effect to take place, the oscillation amplitude must be greater than the atomic radius:

$$\frac{eE_0\tau}{2m\omega_0}\left(1 - \mathrm{e}^{-t/\tau}\right) \geq R_A \, .$$

That sets the threshold field to $2m\omega_0 R_A/(e\tau)$ and the power density of the beam to

$$P = c\epsilon_0 \left(\frac{4\omega_0 m R_A}{\tau e}\right)^2 \sim 100 \text{ W/m}^2 \, ,$$

while the time required to reach the escape amplitude is of the order of τ.

In conclusion, our model predicts a threshold on the power of the beam, but not on its frequency, which however must be tuned to the resonance frequency: the photoelectric effect would cease both below and above the typical resonance frequencies of the atoms in the electrode. Moreover the expectation is that the electron does not gain any further appreciable energy from the electric field once it escapes the atomic bond: hence the emission from the electrode could be strong, but made up of electrons of energy equal to that gained during the last atomic oscillation. Equation (2.14) shows that, during the transient ($t << \tau$), the oscillation amplitude grows roughly by $eE_0/(m\omega_0^2)$ in one period, so that the energy of the escaped electron would be of the order of magnitude of $kR_A eE_0/(m\omega_0^2) = eE_0 R_A$, corresponding also to the energy acquired by the electron from the electric field E_0 when crossing the atom. It is easily computed that for a power density of the order of $10 - 100$ W/m^2, the electric field E_0 is roughly 100 V/m, so that the final kinetic energy of the electron would be 10^{-8} eV $\sim 10^{-27}$ J: this value is much smaller than the typical thermal energy at room temperature ($3kT/2 \sim 10^{-1}$ eV).

The prediction of the model is therefore in clear contradiction with the experimental results described above. In particular the very small energy of the emitted electrons implies that the electric current I should vanish even for small negative potential differences.

Einstein proposed a description of the effect based on the hypothesis that the energy be transferred from the luminous radiation to the electron in a single *elementary* (i.e. no further separable) process, instead than through a gradual excitation. Moreover he proposed that the transferred energy be equal to $h\nu = h\omega/(2\pi) \equiv \hbar\omega$, a quantity called *quantum* by Einstein himself. The constant h had been introduced by Planck several years before to describe the radiation emitted by an oven and its value is 6.63 10^{-34} J s.

If the quantum of energy is enough for electron liberation, i.e. according to our model it is larger than $E_t \equiv kR_A^2/2 = \omega_0^2 R_A^2 m/2 \sim 10^{-19}$ J ~ 1 eV and the frequency exceeds 1.6 10^{14} Hz (corresponding to ω in our model), then the electron is emitted keeping the energy exceeding the threshold in the form of kinetic energy. The number of emitted electrons, hence the intensity of the process, is proportional to the flux of luminous energy, i.e. to the number of quanta hitting the electrode.

Since $E = h\nu$ is the energy gained by the electron, which spends a part E_t to get free from the atom, the final electron kinetic energy is $T = h\nu - E_t$, so that the electric current can be interrupted by placing the second electrode at a negative potential

$$V = \frac{h\nu - E_t}{e} \,,$$

thus reproducing (2.1).

The most important point in Einstein's proposal, which was already noticed by Planck, is that a physical system of typical frequency ν can exchange only quanta of energy equal to $h\nu$. The order of magnitude in the atomic case is $\omega \sim 10^{15}$ s^{-1}, hence $\hbar\omega \equiv (h/2\pi)\,\omega \sim 1$ eV.

2.2 Bohr's Quantum Theory

After the introduction of the concept of a quantum of energy, *quantum theory* was developed by N. Bohr in 1913 and then perfected by A. Sommerfeld in 1916: they gave a precise proposal for multi-periodic systems, i.e. systems which can be described in terms of periodic components.

The main purpose of their studies was that of explaining, in the framework of Rutherford's atomic model, the light spectra emitted by gasses (in particular mono-atomic ones) excited by electric discharges. The most simple and renowned case is that of the mono-atomic hydrogen gas (which can be prepared with some difficulties since hydrogen tends to form bi-atomic molecules). It has a discrete spectrum, i.e. the emitted frequencies can assume only some discrete values, in particular:

$$\nu_{n,m} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \tag{2.15}$$

for all possible positive integer pairs with $m > n$: this formula was first proposed by J. Balmer in 1885 for the case $n = 2$, $m \geq 3$, and then generalized by J. Rydberg in 1888 for all possible pairs (n, m). The emission is particularly strong for $m = n + 1$.

Rutherford had shown that the positive charge in an atom is localized in a practically point-like nucleus, which also contains most of the atomic mass. In particular the hydrogen atom can be described as a two-body system: a heavy and positively charged particle, which nowadays is called proton, bound by Coulomb forces to a light and negatively charged particle, the electron.

We will confine our discussion to the case of circular orbits of radius r, covered with uniform angular velocity ω, and will consider the proton as if it were infinitely heavy (its mass is about $2\ 10^3$ times that of the electron). In this case we have

$$m\omega^2 r = \frac{e^2}{4\pi\epsilon_0 r^2}\,,$$

where m is the electron mass. Hence the orbital frequencies, which in classical physics correspond to those of the emitted radiation, are continuously distributed as a function of the radius

$$\nu = \frac{\omega}{2\pi} = \frac{e}{\sqrt{16\pi^3\epsilon_0 m r^3}}\,, \tag{2.16}$$

this is in clear contradiction with (2.15). Based on Einstein's theory of the photoelectric effect, Bohr proposed to interpret (2.15) by assuming that only certain orbits be allowed in the atom, which are called *levels*, and that the frequency $\nu_{n,m}$ correspond to the transition from the m-th level to n-th one. In that case

$$h\nu_{n,m} = E_m - E_n\,, \tag{2.17}$$

where the atomic energies (which are negative since the atom is a bound system) would be given by

$$E_n = -\frac{hR}{n^2}\,. \tag{2.18}$$

Since, according to classical physics for the circular orbit case, the atomic energy is given by

$$E_{\rm circ} = -\frac{e^2}{8\pi\epsilon_0 r}\,,$$

Bohr's hypothesis is equivalent to the assumption that the admitted orbital radii be

$$r_n = \frac{e^2 n^2}{8\pi\epsilon_0 hR}\,. \tag{2.19}$$

It is clear that Bohr's hypothesis seems simply aimed at reproducing the observed experimental data; it does not permit any particular further development, unless further conditions are introduced. The most natural, which is called *correspondence principle* is that the classical law, given in (2.16), be reproduced by (2.15) for large values of r, hence of n, and at least for the strongest emissions, i.e. those with $m = n + 1$, for which we can write

$$\nu_{n,n+1} = R\frac{2n+1}{n^2(n+1)^2} \to \frac{2R}{n^3}\,, \tag{2.20}$$

these frequencies should be identified in the above mentioned limit with what resulting from the combination of (2.16) and (2.19):

$$\nu = \frac{e}{\sqrt{16\pi^3 \epsilon_0 m r_n^3}} = \frac{2^{\frac{5}{2}} \epsilon_0 (hR)^{\frac{3}{2}}}{e^2 \sqrt{m} n^3} \ . \tag{2.21}$$

By comparing last two equations we get the value of the coefficient R in (2.15), which is called *Rydberg constant*:

$$R = \frac{me^4}{8\epsilon_0^2 h^3}$$

and is in excellent agreement with experimental determinations. We have then the following *quantized* atomic energies

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2 n^2} \ , \qquad n = 1, 2, ...$$

while the quantized orbital radii are

$$r_n = \frac{\epsilon_0 h^2 n^2}{\pi m e^2} \ . \tag{2.22}$$

In order to give a numerical estimate of our results, it is convenient to introduce the ratio $e^2/(2\epsilon_0 hc) \equiv \alpha \simeq 1/137$, which is adimensional and is known as the *fine structure constant.*Constant!fine structure The energy of the state with $n = 1$, which is called the *fundamental state*, is

$$E_1 = -hR = -\frac{mc^2}{2}\alpha^2 \ ;$$

noticing that $mc^2 \sim 0.5\,\mathrm{MeV}$, we have $E_1 \simeq -13$ eV. The corresponding atomic radius is $r_1 \simeq 0.5\ 10^{-10}\,\mathrm{m}$.

Notwithstanding the excellent agreement with experimental data, the starting hypothesis, to be identified with (2.18), looks still quite conditioned by the particular form of Balmer law given in (2.15). For that reason Bohr tried to identify a physical observable to be quantized according to a simpler and more fundamental law. He proceeded according to the idea that such observable should have the same dimensions of the Planck constant, i.e. those of an action, or equivalently of an angular momentum. In the particular case of quantized circular orbits this last quantity reads:

$$L = pr = m\omega r^2 = \frac{e}{\sqrt{4\pi\epsilon_0}}\sqrt{m r_n} = \frac{h}{2\pi} n \equiv n\hbar \ , \qquad n = 1, 2, ... \tag{2.23}$$

2.3 De Broglie's Interpretation

In this picture of partial results, even if quite convincing from the point of view of the phenomenological comparison, the real progress towards understanding quantum physics came as L. de Broglie suggested the existence of a *universal wave-like behavior* of material particles and of energy quanta associated to force fields. As we have seen in the case of electromagnetic waves when discussing the Doppler effect, a phase can always be associated with a wave-like process, which is variable both in space and in time (e.g. given by $2\pi\,(x/\lambda - \nu t)$ in the case of waves moving parallel to the x axis). The assumption that quanta can be interpreted as real particles and that Einstein's law $E = h\nu$ be universally valid, would correspond to identifying the wave phase with $2\pi\,(x/\lambda - Et/h)$. If we further assume the phase to be relativistically invariant, then it must be expressed in the form $(p\ x - E\ t)\,/\hbar$, where E and p are identified with relativistic energy and momentum, i.e. in the case of material particles:

$$E = \frac{mc^2}{\sqrt{\left(1 - \frac{v^2}{c^2}\right)}}\ , \qquad p = \frac{mv}{\sqrt{\left(1 - \frac{v^2}{c^2}\right)}}\ .$$

In order to simplify the discussion as much as possible, we will consider here and in most of the following a one dimensional motion (parallel to the x axis). In conclusion, by comparing last two expressions given for the phase, we obtain de Broglie's equation:

$$p = \frac{h}{\lambda}\ ,$$

which is complementary to Einstein's law, $E = h\nu$.

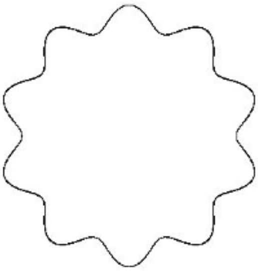
These formulae give an idea of the scale at which quantum effects are visible. For an electron having kinetic energy $E_k = 10^2$ eV $\simeq 1.6\ 10^{-17}$ J quantum effects show up at distances of the order of $\lambda = h/p = h/\sqrt{2mE_k} \sim 10^{-10}$ m, corresponding to atomic or slightly subatomic distances; that confirms the importance of quantum effects for electrons in condensed matter and in particular in solids, where typical energies are of the order of a few electron-Volts. For a gas of light atoms in equilibrium at temperature T, the kinetic energy predicted by equipartition theorem is $3kT/2$, where k is Boltzmann's constant. At a temperature $T = 300$°K (room temperature) the kinetic energy is roughly $2.5\ 10^{-2}$ eV, corresponding to wavelengths of about 10^{-10} m for atom masses of the order of 10^{-26} Kg. However at those distances the picture of a non-interacting (perfect) gas does not apply because of strong repulsive forces coming into play: in order to gain a factor ten on distances, it is necessary to reduce the temperature by a factor 100, going down to a few Kelvin degrees, at which quantum effects are manifest. For a macroscopic body of mass 1 Kg and kinetic energy 1 J quantum effects would show up at distances roughly equal to $3\ 10^{-34}$ m, hence completely negligible with respect to the thermal oscillation amplitudes of atoms, which are proportional to the square root of the absolute temperature, and are in particular of the order of a few nanometers at $T = 10^3$ °K, where the solid melts.

On the other hand, Einstein's formula gives us information about the scale of times involved in quantum processes, which is of the order of $h/\Delta E$, where

ΔE corresponds to the amount of exchanged energy. For $\Delta E \sim 1$ eV, times are roughly 4 10^{-15} s, while for thermal interactions at room temperature time intervals increase by a factor 40.

In conclusion, in the light of de Broglie's formula, quantum effects are not visible for macroscopic bodies and at macroscopic energies. For atoms in matter they show up after condensation or anyway at very low temperatures, while electrons in solids or in atoms are fully in the quantum regime.

In Rutherford's atomic model illustrated in previous Section, the circular motion of the electron around the proton must be associated, according to de Broglie, with a wave closed around the circular orbit. That resembles wave-like phenomena analogous to the oscillations of a ring-shaped elastic string or to air pressure waves in a toroidal reed pipe. That implies well tuned wavelengths, as in the case of musical instruments (which are not ring-shaped for obvious practical reasons). The need for tuned wavelength can be easily understood in the case of the toroidal reed pipe: a complete round of the ring must bring the phase back to its initial value, so that the total length of the pipe must be an integer multiple of the wavelength.



Taking into account previous equations regarding circular atomic orbits, we have the following electron wavelength:

$$\lambda = \frac{h}{p} = \frac{h}{e}\sqrt{\frac{4\pi\epsilon_0 r}{m}} \,,$$

so that the tuning condition reads

$$2\pi r = n\lambda = \frac{nh}{e}\sqrt{\frac{4\pi\epsilon_0 r}{m}}$$

giving

$$r = \frac{n^2 h^2 \epsilon_0}{\pi e^2 m} \,,$$

which confirms (2.22) and gives support to the picture proposed by Bohr and Sommerfeld. De Broglie's hypothesis, which was formulated in 1924, was confirmed in 1926 by Davisson and Gerner by measuring the intensity of an electron beam reflected by a nickel crystal. The apparatus used in the experiment is sketched in Fig. 2.2. The angular distribution of the electrons reflected in conditions of normal incidence shows a strongly anisotropic behavior with a marked dependence on the beam accelerating potential. In particular, an accelerating potential equal to 48 V leads to a quite pronounced peak at a reflection angle $\phi = 55.3°$. An analogous X-ray diffraction experiment permits to interpret the nickel crystal as an atomic lattice of spacing 0.215 10^{-9} m. The comparison between the angular distributions obtained for X-rays and for electrons shows relevant analogies, suggesting a diffractive interpretation also in the case of electrons. Bragg's law giving the n-th maximum in the diffraction figure is $d \sin \phi_n = n\lambda$.

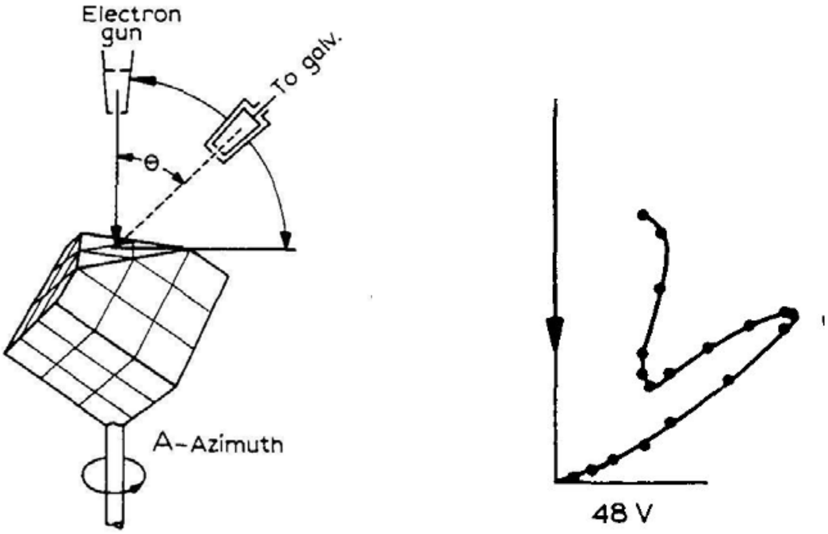


Fig. 2.2. A schematic description of Davisson-Gerner apparatus and a polar coordinate representation of the results obtained at 48 V electron energy, as they appear in Davisson's Noble Price Lecture, from *Nobel Lectures*, Physics 1922-1941 (Elsevier Publishing Company, Amsterdam, 1965)

For the peak corresponding to the principal maximum at 55.3° we have

$$d \ \sin \phi = \lambda \simeq 0.175 \ 10^{-9} \ \mathrm{m}\,.$$

On the other hand the electrons in the beam have a kinetic energy

$$E_k \simeq 7.68 \ 10^{-18} \ \mathrm{J}\,,$$

hence a momentum $p \simeq 3.7 \, 10^{-24}$ N s, in excellent agreement with de Broglie's formula $p = h/\lambda$. In the following years analogous experiments were repeated using different kinds of material particles, in particular neutrons.

Once established the wave-like behavior of propagating material particles, it must be clarified what is the physical quantity the phenomenon refers to, i.e. what is the physical meaning of the oscillating quantity (or quantities) usually called *wave function*, for which a *linear* propagating equation will be supposed, in analogy with mechanical or electromagnetic waves. It is known that, in the case of electromagnetic waves, the quantities measuring the amplitude are electric and magnetic fields. Our question regards exactly the analogous of those fields in the case of de Broglie's waves. The experiment by Davisson and Gerner gives an answer to this question. Indeed, as illustrated in Fig. 2.2, the detector reveals the presence of one or more electrons at a given angle; if we imagine to repeat the experiment several times, with a single electron in the beam at each time, and if we measure the frequency at which electrons are detected at the various angles, we get the *probability* of having the electron in a given site covered by the detector.

In the case of an optical measure, what is observed is the interference effect in the energy deposited on a plate; that is proportional to the square of the electric field on the plate. Notice that the linearity in the wave equation and the quadratic relation between the measured quantity and the wave amplitude are essential conditions for the existence of interference and diffractive phenomena. We must conclude that also in the case of material particles some *positive quadratic form* of de Broglie's wave function gives the probability of having the electron in a given point.

We have quite generically mentioned a quadratic form, since at the moment it is still not clear if the wave function has one or more components, i.e. if it corresponds to one or more real functions. By a positive quadratic form we mean a homogeneous second order polynomial in the wave function components, which is positive for real and non-vanishing values of its arguments. In the case of a single component, we can say without loss of generality that the probability density is the wave function squared, while in the case of two or more components it is always possible, by suitable linear transformations, to reduce the quadratic form to a sum of squares.

We are now going to show that the hypothesis of a single component must be discarded. Let us indicate by $\rho(\boldsymbol{r},t)d^3r$ the probability of the particle being in a region of size d^3r around $\boldsymbol{r}$ at time t, and by $\psi(\boldsymbol{r},t)$ the wave function, which for the moment is considered as a real valued function, defined so that

$$\rho(\boldsymbol{r},t) = \psi^2(\boldsymbol{r},t)\,. \tag{2.24}$$

If Ω indicates the whole region accessible to the particle, the probability density must satisfy the natural constraint:

$$\int_\Omega d^3r\rho\,(\boldsymbol{r},t) = 1\,, \tag{2.25}$$

which implies the condition:

$$\int_\Omega d^3r\,\dot{\rho}(\boldsymbol{r},t) \equiv \int_\Omega d^3r\frac{\partial\rho(\boldsymbol{r},t)}{\partial t} = 0\,. \tag{2.26}$$

This expresses the fact that, if the particle cannot escape Ω, the probability of finding it in that region must always correspond to certainty. This condition can be given in mathematical terms analogous to those used to express electric charge conservation: the charge contained in a given volume, i.e. the integral of the charge density, may change only if the charge flows through the boundary surface. The charge flux through the boundaries is expressed in terms of the current density flow and can be rewritten as the integral of the divergence of the current density itself by using Gauss–Green theorem

$$\int_{\Omega} \dot{\rho} = -\Phi_{\partial\Omega}(J) = -\int_{\Omega} \boldsymbol{\nabla} \cdot \boldsymbol{J} \ .$$

Finally, by reducing the equation from an integral form to a differential one, we can identify the temporal derivative of the charge density with the divergence of the current density. Based on this analogy, let us introduce the *probability current* density $\boldsymbol{J}$ and write

$$\dot{\rho}(\boldsymbol{r},t) = -\frac{\partial J_x(\boldsymbol{r},t)}{\partial x} - \frac{\partial J_y(\boldsymbol{r},t)}{\partial y} - \frac{\partial J_z(\boldsymbol{r},t)}{\partial z} \equiv -\boldsymbol{\nabla} \cdot \boldsymbol{J}(\boldsymbol{r},t)\,. \qquad (2.27)$$

The conservation equation must be automatically satisfied as a consequence of the propagation equation of de Broglie's waves, which we write in the form:

$$\dot{\psi} = L\left(\psi, \boldsymbol{\nabla}\psi, \nabla^2\psi, ..\right) \ , \qquad (2.28)$$

where L indicates a generic linear function of ψ and its derivatives like:

$$L\left(\psi, \boldsymbol{\nabla}\psi, \nabla^2\psi, ..\right) = \alpha\psi + \beta\nabla^2\psi\,. \qquad (2.29)$$

Notice that if L were not linear the interference mechanism upon which quantization is founded would soon or later fail. Furthermore we assume invariance under the reflection of coordinates, so that terms proportional to first derivatives are excluded.

From equation (2.24) we have $\dot{\rho} = 2\psi\dot{\psi}$, which can be rewritten, using (2.28), as:

$$\dot{\rho} = 2\psi L\left(\psi, \boldsymbol{\nabla}\psi, \nabla^2\psi, ..\right) \ . \qquad (2.30)$$

The right-hand side of last equation must be identified with $-\boldsymbol{\nabla}\cdot\boldsymbol{J}(\boldsymbol{r},t)$. Moreover $\boldsymbol{J}$ must necessarily be a bilinear function of ψ and its derivatives exactly like $\dot{\rho}$. Therefore, since $\boldsymbol{J}$ is a vector-like quantity, it must be expressible as

$$\boldsymbol{J} = c\ \psi\boldsymbol{\nabla}\psi + d\ \boldsymbol{\nabla}\psi\nabla^2\psi + \ldots$$

from which it appears that $\boldsymbol{\nabla}\cdot\boldsymbol{J}(\boldsymbol{r},t)$ must necessarily contain bilinear terms in which both functions are derived, like $\boldsymbol{\nabla}\psi\cdot\boldsymbol{\nabla}\psi$: however such terms are clearly missing in (2.30).

We come to the conclusion that the description of de Broglie's waves requires at least two wave functions ψ_1 and ψ_2, defined so that $\rho = \psi_1^2 + \psi_2^2$. In an analogous way we can introduce the complex valued function:

$$\psi = \psi_1 + i\psi_2 \ , \qquad (2.31)$$

defined so that

$$\rho = |\psi|^2 \; ; \tag{2.32}$$

this choice implies:

$$\dot{\rho} = \psi^* \dot{\psi} + \psi \dot{\psi}^* \, .$$

If we assume, for instance, the wave equation corresponding to (2.29):

$$\dot{\psi} = \alpha \psi + \beta \nabla^2 \psi \, , \tag{2.33}$$

we obtain:

$$\dot{\rho} = \psi^* \left(\alpha \psi + \beta \nabla^2 \psi \right) + \psi \left(\alpha^* \psi^* + \beta^* \nabla^2 \psi^* \right) \; .$$

If we also assume that the current probability density be

$$\boldsymbol{J} = \mathrm{i} k \left(\psi^* \boldsymbol{\nabla} \psi - \psi \boldsymbol{\nabla} \psi^* \right) \; , \tag{2.34}$$

with k real so as to make $\boldsymbol{J}$ real as well, we easily derive

$$\boldsymbol{\nabla} \cdot \boldsymbol{J} = \mathrm{i} k \left(\psi^* \nabla^2 \psi - \psi \nabla^2 \psi^* \right) \; .$$

It can be easily verified that the continuity equation (2.27) is satisfied if

$$\alpha + \alpha^* = 0 \, , \qquad \beta = -\mathrm{i} k \, . \tag{2.35}$$

It is of great physical interest to consider the case in which the wave function has more than two real components. In particular, the wave function of electrons has four components or, equivalently, two complex components. In general, the multiplicity of the complex components is linked to the existence of an intrinsic angular momentum, which is called *spin*. The various complex components are associated with the different possible spin orientations. In the case of particles with non-vanishing mass, the number of components is $2S+1$, where S is the spin of the particle. In the case of the electron, $S = 1/2$.

For several particles, as for the electron, spin is associated with a magnetic moment which is inherent to the particle: it behaves as a microscopic magnet with various possible orientations, corresponding to those of the spin, which can be selected by placing the particle in a non-uniform magnetic field and measuring the force acting on the particle.

2.4 Schrödinger's Equation

The simplest case to which our considerations can be applied is that of a non-relativistic free particle of mass m. To simplify notations and computations, we will confine ourselves to a one-dimensional motion, parallel for instance, to the x axis; if the particle is not free, forces will be parallel to the same axis as well. The obtained results will be extensible to three dimensions by exploiting the vector formalism. In practice, we will sistematically replace $\boldsymbol{\nabla}$ by its component $\nabla_x = \partial / \partial x \equiv \partial_x$ and the Laplacian operator $\nabla^2 =$

$\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ by $\partial^2/\partial x^2 \equiv \partial_x^2$; the probability current density $\boldsymbol{J}$ will be replaced by J_x (J) as well. The inverse replacement will suffice to get back to three dimensions.

The energy of a non-relativistic free particle is

$$E = c\sqrt{m^2c^2 + p^2} \simeq mc^2 + \frac{p^2}{2m} + O\left(\frac{p^4}{m^3c^2}\right) ,$$

where we have explicitely declared our intention to neglect terms of the order of $p^4/(m^3c^2)$. Assuming de Broglie's interpretation, we write the wave function:

$$\psi_P(x,t) \sim \mathrm{e}^{2\pi \mathrm{i}(x/\lambda - \nu t)} = \mathrm{e}^{\mathrm{i}(px - Et)/\hbar} \tag{2.36}$$

(we are considering a motion in the positive x direction). Our choice implies the following wave equation

$$\dot{\psi}_P = -\frac{\mathrm{i}E}{\hbar}\psi_P = -\frac{\mathrm{i}}{\hbar}\left(mc^2 + \frac{1}{2m}p^2\right)\psi_P \, . \tag{2.37}$$

We have also

$$\partial_x \psi_P = \frac{\mathrm{i}}{\hbar} p \psi_P \, , \tag{2.38}$$

from which we deduce

$$\mathrm{i}\hbar\dot{\psi}_P = mc^2\psi_P - \frac{\hbar^2}{2m}\partial_x^2\psi_P \, . \tag{2.39}$$

Our construction can be simplified by multiplying the initial wave function by the phase factor $\mathrm{e}^{\mathrm{i}mc^2t/\hbar}$, i.e. defining

$$\psi \equiv \mathrm{e}^{\mathrm{i}mc^2t/\hbar}\psi_P \sim \exp\left(\frac{\mathrm{i}}{\hbar}\left(px - \frac{p^2}{2m}t\right)\right) \, . \tag{2.40}$$

Since the dependence on x is unchanged, ψ still satisfies (2.38) and has the same probabilistic interpretation as ψ_P. Indeed both ρ and J are unchanged. The wave equation instead changes:

$$\mathrm{i}\hbar\dot{\psi} = -\frac{\hbar^2}{2m}\partial_x^2\psi \equiv T\psi \, . \tag{2.41}$$

This is the *Schrödinger equation* for a free (non-relativistic) particle, in which the right-hand side has a natural interpretation in terms of the particle energy, which in the free case is only of kinetic type.

In the case of particles under the influence of a force field corresponding to a potential energy $V(x)$, the equation can be generalized by adding $V(x)$ to the kinetic energy :

$$\mathrm{i}\hbar\dot{\psi} = -\frac{\hbar^2}{2m}\partial_x^2\psi + V(x)\psi \, . \tag{2.42}$$

This is the one-dimensional Schrödinger equation that we shall apply to various cases of physical interest.

Equations (2.34) and (2.35) show that the probability density current does not depend on V and is given by:

$$J = -\frac{\mathrm{i}\hbar}{2m}\left(\psi^* \partial_x \psi - \psi \partial_x \psi^*\right) . \tag{2.43}$$

Going back to the free case and considering the *plane* wave function given in (2.36), it is interesting to notice that the corresponding probability density, $\rho = |\psi|^2$, is a constant function. This result is paradoxical since, by reducing (2.25) to one dimension, we obtain

$$\int_{-\infty}^{\infty} dx\ \rho(x,t) = \int_{-\infty}^{\infty} dx\ |\psi(x,t)|^2 = 1\ , \tag{2.44}$$

which cannot be satisfied in the examined case since the integral of a constant function is divergent. We must conclude that our interpretation excludes the possibility that a particle have a well defined momentum.

We are left with the hope that this difficulty may be overcome by admitting some (small) uncertainty on the knowledge of momentum. This possibility can be easily analyzed thanks to the linearity of Schrödinger equation. Indeed equation (2.41) admits other different solutions besides the simple plane wave, in particular the *wave packet* solution, which is constructed as a linear superposition of many plane waves according to the following integral:

$$\int_{-\infty}^{\infty} dp\ \tilde{\psi}(p) \exp\left(\frac{\mathrm{i}}{\hbar}\left(px - \frac{p^2}{2m}t\right)\right) .$$

The squared modulus of the superposition coefficients, $|\tilde{\psi}(p)|^2$, can be naturally interpreted, apart from a normalization constant, as the probability density in terms of momentum, exactly in the same way as $\rho(x)$ is interpreted as a probability density in terms of position.

Let us choose in particular a Gaussian distribution:

$$\tilde{\psi}(p) \sim \mathrm{e}^{-(p-p_0)^2/(4\Delta^2)}\ , \tag{2.45}$$

corresponding to

$$\psi_\Delta(x,t) = k \int_{-\infty}^{\infty} dp\ \mathrm{e}^{-(p-p_0)^2/(4\Delta^2)}\ \mathrm{e}^{\mathrm{i}\left(px - p^2 t/2m\right)/\hbar} . \tag{2.46}$$

where k must be determined in such a way that $\int_{-\infty}^{\infty} dx |\psi_\Delta(x,t)|^2 = 1$.

The integral in (2.46) can be computed by recalling that, if α is a complex number with positive real part ($Re\ (\alpha) > 0$), then

$$\int_{-\infty}^{\infty} dp\ \mathrm{e}^{-\alpha p^2} = \sqrt{\frac{\pi}{\alpha}}$$

and that the Riemann integral measure dp is left invariant by translations in the complex plane,

$$\begin{aligned}\int_{-\infty}^{\infty} dp\ \mathrm{e}^{-\alpha p^2} &\equiv \int_{-\infty}^{\infty} d(p+\gamma)\ \mathrm{e}^{-\alpha(p+\gamma)^2} \\ &= \int_{-\infty}^{\infty} dp\ \mathrm{e}^{-\alpha(p+\gamma)^2} = \mathrm{e}^{-\alpha\gamma^2}\int_{-\infty}^{\infty} dp\ \mathrm{e}^{-\alpha p^2}\mathrm{e}^{-2\alpha\gamma p}\,,\end{aligned}$$

for every complex number γ. Therefore we have

$$\int_{-\infty}^{\infty} dp\ \mathrm{e}^{-\alpha p^2}\mathrm{e}^{\beta p} = \sqrt{\frac{\pi}{\alpha}}\mathrm{e}^{\beta^2/4\alpha}\,. \tag{2.47}$$

Developing (2.46) with the help of (2.47) we can write

$$\begin{aligned}\psi_\Delta(x,t) &= k\mathrm{e}^{-\frac{p_0^2}{4\Delta^2}}\int_{-\infty}^{\infty} dp\ \mathrm{e}^{-\left[\frac{1}{4\Delta^2}+\frac{\mathrm{i}t}{2m\hbar}\right]p^2}\ \mathrm{e}^{\left[\frac{p_0}{2\Delta^2}+\frac{\mathrm{i}x}{\hbar}\right]p} \\ &= k\sqrt{\frac{\pi}{\frac{1}{4\Delta^2}+\frac{\mathrm{i}t}{2m\hbar}}}\ \exp\left(\frac{\left[\frac{p_0}{2\Delta^2}+\frac{\mathrm{i}x}{\hbar}\right]^2}{\frac{1}{\Delta^2}+\frac{2\mathrm{i}t}{m\hbar}} - \frac{p_0^2}{4\Delta^2}\right)\,.\end{aligned} \tag{2.48}$$

We are interested in particular in the x dependence of the probability density $\rho(x)$: that is solely related to the real part of the exponent of the rightmost term in (2.48), which can be expanded as follows:

$$\frac{\frac{p_0^2}{4\Delta^4}+\frac{\mathrm{i}p_0x}{\Delta^2\hbar}-\frac{x^2}{\hbar^2}}{\frac{1}{\Delta^2}+\frac{2\mathrm{i}t}{m\hbar}} - \frac{p_0^2}{4\Delta^2} = -\frac{p_0^2}{4\Delta^2}\frac{\frac{4t^2\Delta^4}{m^2\hbar^2}+\frac{2\mathrm{i}t\Delta^2}{m\hbar}}{1+\frac{4t^2\Delta^4}{m^2\hbar^2}} - \left(\frac{\Delta^2x^2}{\hbar^2}-\frac{\mathrm{i}p_0x}{\hbar}\right)\frac{1-\frac{2\mathrm{i}t\Delta^2}{m\hbar}}{1+\frac{4t^2\Delta^4}{m^2\hbar^2}}$$

the real part being

$$-\frac{\Delta^2\left(x-\frac{p_0t}{m}\right)^2}{\hbar^2\left(1+\frac{4t^2\Delta^4}{m^2\hbar^2}\right)} \equiv -\frac{\Delta^2\left(x-v_0t\right)^2}{\hbar^2\left(1+\frac{4t^2\Delta^4}{m^2\hbar^2}\right)}\,.$$

Since p_0 is clearly the average momentum of the particle, we have introduced the corresponding average velocity $v_0 = p_0/m$. Recalling the definition of ρ as well as its normalization constraint, we finally find

$$\rho(x,t) = \frac{\Delta}{\hbar}\sqrt{\frac{2}{\pi\left(1+\frac{4t^2\Delta^4}{m^2\hbar^2}\right)}}\exp\left(-\frac{2\Delta^2}{\hbar^2}\frac{\left(x-v_0t\right)^2}{1+\frac{4t^2\Delta^4}{m^2\hbar^2}}\right)\,, \tag{2.49}$$

while the probability distribution in terms of momentum reads

$$\tilde{\rho}(p) = \frac{1}{\sqrt{2\pi}\Delta}\mathrm{e}^{-(p-p_0)^2/(2\Delta^2)}\,. \tag{2.50}$$

Given a Gaussian distribution $\rho(x) = 1/(\sqrt{2\pi}\sigma)\mathrm{e}^{-(x-x_0)^2/(2\sigma^2)}$, it is a well known fact, which anyway can be easily derived from previous formulae, that the mean value $\bar{x}$ is x_0 while the mean quadratic deviation $\overline{(x-\bar{x})^2}$ is equal to σ^2. Hence, in the examined case, we have an average position $\bar{x} = v_0 t$ with a mean quadratic deviation equal to $\hbar^2/(4\Delta^2) + t^2\Delta^2/m^2$, while the average momentum is p_0 with a mean quadratic deviation Δ^2. The mean values represent the kinematic variables of a free particle, while the mean quadratic deviations are roughly inversely proportional to each other: if we improve the definition of one observable, the other becomes automatically less defined.

The distributions given in (2.49) and (2.50), even if derived in the context of a particular example, permit to reach important general conclusions which, for the sake of clarity, are listed in the following as distinct points.

2.4.1 The Uncertainty Principle

While the mean quadratic deviation relative to the momentum distribution

$$\overline{(p-\bar{p})^2} = \Delta^2$$

has been fixed a-priori by choosing $\tilde{\psi}(p)$ and is independent of time, thus confirming that momentum is a constant of motion for a free particle, that relative to the position

$$\overline{(x-\bar{x})^2} = \left(1 + \frac{4t^2\Delta^4}{m^2\hbar^2}\right)\frac{\hbar^2}{4\Delta^2}$$

does not contain further free parameters and does depend on time. Indeed, Δ_x grows significantly for $2t\Delta^2/(m\hbar) > 1$, hence for times greater than $t_s = m\hbar/(2\Delta^2)$. Notice that t_s is nothing but the time needed for a particle of momentum Δ to cover a distance $\hbar/(2\Delta)$, therefore this spreading has a natural interpretation also from a classical point of view: a set of independent particles having momenta distributed according to a width Δ_p, spreads with velocity $\Delta_p/m = v_s$; if the particles are statistically distributed in a region of size initially equal to Δ_x, the same size will grow significantly after times of the order of Δ_x/v_s.

What is new in our results is, first of all, that they refer to a single particle, meaning that uncertainties in position and momentum are not avoidable; secondly, these uncertainties are strictly interrelated. Without considering the spreading in time, it is evident that the uncertainty in one variable can be diminished only as the other uncertainty grows. Indeed, Δ can be eliminated from our equations by writing the inequality:

$$\Delta_x\Delta_p \equiv \sqrt{\overline{(x-\bar{x})^2}\ \overline{(p-\bar{p})^2}} \geq \frac{\hbar}{2}\,, \tag{2.51}$$

which is known as the *Heinsenberg uncertainty principle* and can be shown to be valid for any kind of wave packet. The case of a real Gaussian packet corresponds to the minimal possible value $\Delta_x\Delta_p = \hbar/2$.

From a phenomenological point of view this principle originates from the universality of diffractive phenomena. Indeed diffractive effects are those which prevent the possibility of a simultaneous measurement of position and momentum with arbitrarily good precision for both quantities. Let us consider for instance the case in which the measurement is performed through optical instruments; in order to improve the resolution it is necessary to make use of radiation of shorter wavelength, thus increasing the momenta of photons, which hitting the object under observation change its momentum in an unpredictable way. If instead position is determined through mechanical instruments, like slits, then the uncertainty in momentum is caused by diffractive phenomena.

It is important to evaluate the order of magnitude of quantum uncertainty in cases of practical interest. Let us consider for instance a beam of electrons emitted by a cathode at a temperature $T = 1000°\mathrm{K}$ and accelerated through a potential difference equal to 10^4 V. The order of magnitude of the kinetic energy uncertainty Δ_E is kT, where $k = 1.381\ 10^{-23}$ J/°K is the Boltzmann constant (alternatively one can use $k = 8.617\ 10^{-5}$ eV/°K). Therefore $\Delta_E = 1.38\ 10^{-20}$ J while $E = 1.6\ 10^{-15}$ J, corresponding to a quite precise determination of the beam energy ($\Delta_E/E \sim 10^{-5}$). We can easily compute the momentum uncertainty by using error propagation ($\Delta_p/p = \frac{1}{2}\Delta_E/E$) and computing $p = \sqrt{2m_e E} = 5.6\ 10^{-23}$ N s; we thus obtain $\Delta_p = 2.8\ 10^{-28}$ N s, hence, making use of (2.51), $\Delta_x \geq 2\ 10^{-7}$ m. It is clear that the uncertainty principle does not place significant constraints in the case of particle beams.

A macroscopic body of mass $M = 1$ Kg placed at room temperature ($T \simeq 300°\mathrm{K}$) has an average thermal momentum , caused by collisions with air molecules, which is equal to $\Delta_p \sim \sqrt{2M\ 3kT/2} \simeq 9\ 10^{-11}$ N s, so that the minimal quantum uncertainty on its position is $\Delta_x \sim 10^{-24}$ m, hence not appreciable.

The uncertainty principle is instead quite relevant at the atomic level, where it is the stabilizing mechanism which prevents the electron from collapsing onto the nucleus. We can think of the electron orbital radius as a rough estimate of its position uncertainty ($\Delta_x \sim r$) and evaluate the kinetic energy deriving from the momentum uncertainty; we have $E_k \sim \Delta_p^2/(2m) \sim \hbar^2/(2mr^2)$. Taking into account the binding Coulomb energy, the total energy is

$$E(r) \sim \frac{\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}\,.$$

We infer that the system is stable, since the total energy $E(r)$ has an absolute minimum. The stable radius r_m corresponding to this minimum can be computed through the equation

$$\frac{e^2}{4\pi\epsilon_0 r_m^2} - \frac{\hbar^2}{m r_m^3} = 0\,,$$

hence