Chapter 23

Otto Stern and Wave-Particle Duality

J. Peter Toennies

Abstract The contributions of Otto Stern to the discovery of wave-particle duality of matter particles predicted by de Broglie are reviewed. After a short introduction to the early matter-vs-wave ideas about light, the events are highlighted which lead to de Broglie's idea that all particles, also massive particles, should exhibit wave behavior with a wavelength inversely proportional to their mass. The first confirming experimental evidence came for electrons from the diffraction experiments of Davisson and Germer and those of Thomson. The first demonstration for atoms, with three orders of magnitude smaller wave lengths, came from Otto Stern's laboratory shortly afterwards in 1929 in a remarkable *tour de force* experiment. After Stern's forced departure from Hamburg in 1933 it took more than 40 years to reach a similar level of experimental perfection as achieved then in Stern's laboratory. Today He atom diffraction is a powerful tool for studying the atomic and electronic structure and dynamics of surfaces. With the advent of nanotechnology nanoscopic transmission gratings have led to many new applications of matter waves in chemistry and physics, which are illustrated with a few examples and described in more detail in the following chapters.

1 Introduction

On September 8, 1926 Otto Stern submitted the first of a projected series of 30 articles all of which were to appear in the *Zeitschrift für Physik* under the subtitle "Untersuchungen zur Molekularstrahlmethode (UzM) aus dem Institut für physikalische Chemie der Hamburgischen Universität" [1]. In this initial article he outlined his plans for future physics experiments based on the method of molecular beams. It is remarkable that almost all of the projected experiments were successfully carried out in the ensuing 7 years until 1933 when Stern was forced to leave Germany. At the end of the list he had two special projects: "Der Einsteinsche Strahlungsdruck"

J. Peter Toennies (✉)
Max-Planck-Institut für Dynamik und Selbstorganisation, Am Fassberg 17, 37077 Göttingen,
Germany
e-mail: jtoenni@gwdg.de

and “Die De Broglie-Wellen”. Two years earlier, on November 1924, a little known young French physicist, Louis de Broglie, had defended his Sorbonne thesis [2]. In his thesis he published his famous formula $\lambda = h/mv$ ¹ which introduced, for the first time, the concept of wave-particle duality of massive particles. Thus in 1926 Otto Stern was among the first who realized the tremendous importance of confirming de Broglie’s revolutionary ideas by experiment.

After several marginally successful experiments, in May 1929 Otto Stern reported in a short note in the journal *Naturwissenschaften* well-resolved diffraction peaks in the reflection of He atoms from a cleaved NaCl crystal surfaces [3]. Thereby he provided the first direct evidence that the incident atoms of helium as massive particles had wave properties. Earlier in 1927, at about the same time as Stern and colleagues were still optimizing their experiment, Davisson and Germer had reported the first experimental evidence for the wave nature of electrons in *Nature* [4]. In the same year the wave nature of electrons was also independently confirmed in another *Nature* article by Thomson and Reid [5].

In the following, the history of the genesis of wave-particle duality will be reviewed. Then the diffraction experiments of Otto Stern will be described in more detail. Recent He atom diffraction experiments following on the footsteps of Stern and based partly on new developments are reviewed. These will serve as an introduction to the following articles describing the current state of experiments made possible by nanotechnologic advances which rely on the wave-particle duality of atoms and molecules.

2 History of Wave-Particle Duality and the de Broglie Relation

The early Greek philosophers Leucippus (fifth century BC) and his pupil Democritus (c. 460–c. 370 BC) were probably the first to introduce the idea that matter is composed of atoms (Greek for indivisible). Some of the early Greek philosophers also supposed that the *seen* object was emitting particles that bombarded their eyes. A modern theory that light was made of particles was first formulated much later by Isaac Newton (1643–1727). Somewhat earlier the idea that light was made of waves was postulated by Huygens (1629–1695). Soon after Thomas Young (1773–1829), August Jean Fresnel (1778–1827) and Joseph von Fraunhofer (1778–1826) carried out experiments which confirmed the wave nature of light. The wave versus particle dichotomy of light persisted up to the twentieth century. At the turn of the century, in 1900, Max Planck (1858–1947) introduced his famous radiation law and introduced the concept of a quantum of light which led the way to the development of Quantum Mechanics in 1926.

The modern development of the concept of matter waves can be traced back to 1905 when Einstein (1879–1955) used Planck’s constant to explain the photoelectric

¹ λ is the wave length of a particle with mass m moving at velocity v . h is Planck’s constant.

effect with the simple equation

$$KE_{el} = h\nu - \phi, \quad (1)$$

where KE_{el} is the kinetic energy of the ejected electron, ν is the frequency of the incident photons, and ϕ is the work function of the solid. Thereby it was established that photons act like particles with a fixed energy. Some years later, in 1923, Arthur Compton (1892–1962) reported that the X-ray photons that had been scattered from an electron in a solid, had a fixed momentum $P_{ph} = mc = \frac{h\nu}{c}$. Moreover, the momentum of the rebounding electrons could be explained by conservation of momentum and energy by assuming that the incident X-ray was a particle.

In 1919, these developments attracted the attention of Louis de Broglie (1892–1987) after he had been released from the army after World War I. Working in the laboratory of his physicist brother he became interested in the new concept of a “quanta of light”. In 1922 he published two short articles on black-body radiation [6, 7]. Then, in 1923 he published three additional short two-page articles in *Comptes Rendus* [8] in which he developed his ideas on the wave nature of light. These he summarized in a half-page *Nature* article in 1923 [9] and in the Philosophical Magazine [10]. In the *Nature* article he concluded: “A radiation of frequency ν has to be considered as divided into atoms of light of very small internal mass ($< 10^{-50}$ gm) which move with a velocity very nearly equal to c given by $\frac{m_0 c^2}{\sqrt{1-\beta^2}} = h\nu$. The atom of light slides slowly upon the non-material wave the frequency of which is ν and velocity c/β , very little higher than c . The phase wave has a very great importance in determining the motion of any moving body, and I have been able to show that the stability conditions of the trajectories in Bohr’s atom express that the wave is tuned with the length of the closed path.” With this he anticipated his wave hypothesis in the case of the electron orbits in an atom by showing that the circumference of the orbits would be an integral multiple of the wavelength of the electron.

De Broglie’s *These de doctoral* appeared in the following year 1924 and later was published in 1925 in *Annales de Physique* [11]. In only one place in the final short chapter in one of the last sections entitled *The New Conception of Gas Equilibrium* he writes his famous formula

$$\lambda = \frac{h}{m\nu}. \quad (2)$$

The fact that the formula appears only once suggests that at the time he was apparently more interested in discussing wave motion in general as applied to X-rays and electrons and did not fully realize then the far-reaching significance of the equation for which he is presently known.

According to the excellent reviews of de Broglie’s discovery by Medicus [12] and MacKinnan [13] de Broglie’s work did not become widely known, partly because *Comptes Rendus* was not very popular and partly because the reputation of the little-known young theoretician was controversial. De Broglie’s thesis only became widely

known after Paul Langevin, who was a member of his examination committee, had sent it to Einstein. Einstein immediately appreciated the far reaching consequences of de Broglie's ideas and wrote back that de Broglie had "lifted a corner of the great veil" and incorporated the new concept in his article in the *Proceedings of the Prussian Academy* which appeared in 1925 [14].

3 1925: Experimental Confirmation for Electrons

About the time of de Broglie's theories Clinton J. Davisson at the American Telephone and Telegraph (now AT&T) and the Western Electric Company in New York City was experimenting on the effect of electron bombardment on metal surfaces. This research was carried out in connection with understanding the physics of vacuum tubes which were a major product of the two companies. In 1921, Davisson and Kunsman had reported their initial results on the measurements of the angular distributions of scattered electrons with incident energies up to 1000 eV in *Science* [15] and later in *Physical Review* [16]. At energies below 125 eV upon scattering from platinum and magnesium metal surfaces, they observed an unexpected small lobe in an otherwise Gauss-shaped distribution (Fig. 1). The lobe, they thought, could be related to the Bohr-model electron orbits in the metal.

Fig. 1 The angular distribution of scattered electrons from nickel observed by Davisson and Kunsman in 1921. The figure is taken from Ref. [16]

In the summer of 1925, in far away Göttingen, Friedrich Hund (1896–1997) gave a talk about the experiments of Davisson and Kunsman in Prof. Max Born's seminar on *Die Struktur der Materie*. The Göttingen physicists were then also interested in electron scattering in connection with the 1924 Franck-Hertz experiment, which Franck and Hertz had carried out in Berlin before coming to Göttingen. In Göttingen it was one of the areas of research of the Born group. Walter Elsasser (1904–1942), a student attending the seminar, who had read about de Broglie's theory which had appeared in the same year, conjectured that the lobes reported by Davisson and Kunsman were in fact partly resolved diffraction peaks and could be the first experimental confirmation of de Broglie's theory. Since Elsasser was also attending the lecture course given by Prof. James Franck (1882–1964), he told Franck about his thoughts, whereupon Franck encouraged Elsasser to write a short article about his idea (Fig. 2). The half-page letter appeared in August 1925 in *Die Naturwissenschaften* [17].

The previous account is from the American National Academy of Sciences Biographical Memoir about Elsasser written by Rubin [18]. The important role of Elsasser is also supported by Hund [19] and also by Max Born in his article on the quantum mechanics of collisions [20]. Later, however, Max Born claimed that he had the idea and that he was the one to encourage Elsasser to write the note [21]. In the same article he does remark that he cannot fully remember the details. A somewhat

W. Elsasser
1904-1942

1925 Walter Elsasser, a student in Born's Seminar „Die Struktur der Materie“ heard a talk by Frederick Hund about the experiments of Davisson and Kunsman

F. Hund
1896-1997

Walter came up with the idea that this could be evidence for de Broglie's idea of matter waves.

J. Franck
1882-1964

James Franck suggested to Walter that he should submit an article to the journal *Die Naturwissenschaften*. The short note appeared on July 18, 1925. Thus Elsasser was the first to point to experiments confirming de Broglie's ideas

Fig. 2 The story behind the first realization of experimental evidence for wave-particle duality according to the official National Academy of Science biography of Walter Elsasser [18]

different story can be found in Gehrenberg [22, 23]. It is also interesting to note that Davisson and his assistant Germer were not at all convinced by Elsasser's idea. In their 1927 article in *Physical Review* [24] they wrote "We would like to agree with Elsasser in his interpretation of the small lobe reported by Davisson and Kunsman in 1921 and 1923, but are unable to do so". At the time they were convinced that the curves seen in their initial experiments were "unrelated to crystal structure".

At about the same time, in April 1925, a momentous accident occurred in the laboratory of Clinton Davisson. The glass vacuum tube containing the electron scattering apparatus exploded while the metal target was at high temperatures. In an attempt to save the highly oxidized target it was subsequently baked out over an extended period of time in an effort to reduce the oxide coating. When the experiments were repeated, surprisingly, much sharper lobes were observed, which were especially apparent when the crystal was rotated in the azimuthal direction (Fig. 3). In their *Nature* article in 1927 [4] Davisson and Germer attributed the six sharp azimuthal features to matter-wave diffraction in agreement with the theory of de Broglie. In this same article they do finally give credit to Elsasser. In the same year they published a complete analysis in *Physical Review* [24]. There they attributed the appearance of the newly found diffraction peaks to the increased order of the sample, which had been partly crystallized by the annealing during the long bake out [24]. With serendipitous good fortune, they had finally succeeded in providing convincing confirmation of the

Fig. 3 The first unequivocal evidence for the de Broglie formula came from the 1927 electron diffraction experiments of Davisson and Germer (a). b The polar angle distribution shows diffraction peaks on both sides of the specularly reflected beam. c Schematic diagram of the electron scattering apparatus. d The sharp diffraction peaks observed on rotating the crystal. The latter 3 figures are from Ref. [24]

de Broglie relation. Of course this brief account does not in any way do justice to the many agonizing attempts that finally led to Davisson and Germer's accidental but successful experiment. The full story has been documented in detail by Gehrenberg [22].

This pioneering experiment was the forerunner of modern *Low Energy Electron Diffraction (LEED)* and *Electron Energy Loss Spectroscopy (EELS)* methods for surface analysis. Presently the former is widely used to determine the structure mostly of metal surfaces and the latter for measuring the surface phonons and the vibrations of clean and adsorbate-covered surfaces.

Then also in 1925, George P. Thomson (1892–1975), the son of the famous English physicist J. J. Thomson, reported on the diffraction of high energy electron beams (3,900–16,500 eV) upon passage through a 30 nm thick celluloid film. Their *Nature* article [8] appeared only two months after the *Nature* article of Davisson and Germer. With their simple but elegant experiment they were able to also verify the de Broglie relation (Fig. 4) [25]. In 1937, both Davisson and Thomson were awarded the Nobel Prize for *The Discovery of the Electron Waves*.

The significance of these developments has recently been highlighted in a thought provoking article by Steven Weinberg entitled *The Trouble with Quantum Mechanics* [27]. He begins his *critique* of quantum mechanics by noting “Then in the 1920s, according to theory of Louis de Broglie and Erwin Schrödinger, it appeared that

Fig. 4 The electron transmission experiment by G. P. Thomson which appeared a few months after the results of Davisson and Germer. **a** Photo of G. P. Thomson. **b** Diffraction rings on transmission through celluloid. **c** The electron transmission apparatus. **d** Diffraction rings seen on transmission through two different thin gold foils. The later 3 figures are from Ref. [26]

electrons which had always been recognized as particles, under some circumstances behaved as waves. In order to account for the energies of the stable states of atoms, physicists had to give up the notion that electrons in atoms are little Newtonian planets in orbit around the atomic nucleus. Electrons in atoms are better described as waves, fitting into an organ pipe. The world's categories had become all muddled."

4 Otto Stern's Experimental Confirmation for Atoms

Otto Stern's career as an experimentalist started in 1919 when he took up the position of assistant in Max Born's two-room theory group at the University of Frankfurt [28]. With a cleverly conceived apparatus he was able, for the first time, to measure the mean velocity in a molecular beam, which had been predicted by Clausius [29]. Then, in 1921 he embarked with Walter Gerlach on the famous Stern-Gerlach experiment [30], which led to the discovery of angular momenta and magnetic moments of atoms in magnetic fields. In the fall of the same year, Stern left Frankfurt to take up a new position as "Extraordinarius" (associate professor) at the University of Rostock. In the aftermath of World War I, the financial conditions in Rostock were such that he could not think of carrying out experimental research. Fortunately, Stern's Rostock period lasted only one year. In the following fall of 1922 he accepted an offer as an "Ordinarius" (full professor) of Physical Chemistry and Director of the Institute of Physical Chemistry at the University of Hamburg. On January 1, 1923, in the midst of the great inflation in Germany, he took up his research activities at Hamburg. Here Stern had the good fortune to be assigned four laboratory rooms in the basement of the Physics Institute. Now Stern was finally able to continue the experiments started in Frankfurt and to plan new molecular beam experiments.

Then, as already mentioned in the Introduction, on September 8, 1925 Otto Stern's manifesto appeared in *Zeitschrift für Physik* in which he outlined his plans for future molecular beam experiments including the confirmation of the de Broglie relation [19]. In this connection, he wrote (translated by the author) "...A question of great principle importance is the real existence of de Broglie waves, i.e. the question if with molecular beams, in analogy to light beams, diffraction and interference phenomena can be observed. Unfortunately, the wave lengths calculated with the formula of de Broglie ($\lambda = \frac{h}{m \cdot v}$), even under the most favorable conditions (small mass and low temperatures), are less than 1 Å ($=10^{-1}$ nm). Nevertheless, the possibility in such an experiment to observe these phenomena cannot be excluded. Such experiments have so far not been successful." In a footnote he noted that at the time when they started their experiments in Hamburg he was not aware of the 1927 experiments of Davisson and Germer.

The report on the first experiments, which were judged publishable, was submitted on Christmas eve of 1928 as publication No. 11 in the series *Untersuchungen zur Molekularstrahlmethode* (UzM) with Friedrich Knauer [31]. In this initial experiment molecular beams of H₂ and He were scattered under grazing angles of only 10^{-3}

Fig. 5 The first experiment by Stern for a test of the de Broglie relation for massive particles. **a** A schematic diagram of the apparatus taken from the publication Ref. [31]. **b** A photo of a typical glass vacuum apparatus used by Stern and his colleagues

radians from a flat ruled optical grating made either of brass, glass or steel with up to 100 grooves per mm (Fig. 5). These experiments were only partially successful in the sense that only a sharp specular reflected beam but no diffracted beams were observed. The latter, it was concluded, were too close to the specular peak to be resolved. In the same article they describe a second apparatus which was designed for scattering at large angles. With this apparatus they scattered various atoms and molecules including H_2 , He, Ne, Ar and CO_2 from a freshly cleaved and continually heated (100 C) NaCl crystal. At the time it was well established that the ionic alkali halide crystals were easily cleaved and that the resulting surfaces were relatively free of defects. Again, only for H_2 and He could relatively sharp specular scattering be observed. In the same UzM article they noted that parallel research was going on in the U.S. by Johnson [32] who had reported a specular peak with H atoms scattered from LiF and Ellet and Olsen [33] who scattered Cd and Hg atoms from NaCl, and that they had also been unsuccessful in observing diffraction.

Several months later on April 20, 1929, as mentioned in the Introduction, Otto Stern submitted a short note to the *Naturwissenschaften* reporting that with the second apparatus he had now found convincing evidence for the sought-after diffraction peaks with both He and H_2 in scattering from the surface of a single crystal of NaCl [6]. One year later, Immanuel Estermann and Otto Stern in UzM No. 15 reported that with an improved apparatus they were now able to observe well-resolved diffraction peaks both with H_2 and He from LiF, NaCl and KCl [34] (Fig. 6). The diffraction angles obeyed the de Broglie relation ($\lambda = \frac{h}{m \cdot v}$) calculated from the lattice constants of the crystals and the masses of the scattering particles, both of which were well-known at the time.

Apparently, Otto Stern was still not completely satisfied judging by the fact that in the following year in 1930 he embarked on an ambitious project to rigorously and quantitatively check the de Broglie relation. For this it was necessary to use a beam with a well-defined velocity. In the following pioneering experiments two

Fig. 6 The first successful diffraction of a massive particle, He from crystalline LiF observed by Stern in 1929 [3]. **a** The glass encased vacuum apparatus in which the crystal was rotated. **b** The diffraction pattern showing two first order diffracted peaks on both sides of the specular peak [34]

new methods were used to select velocities from the broad Maxwell-Boltzmann distribution [34]. One method exploited the dependence of the first order diffraction angle on the incident beam velocity. In this apparatus, the He atom beam was first diffracted from one crystal surface and only those atoms diffracted into a chosen solid angle, corresponding to the desired velocity, were transmitted. These atoms were then directed at the second crystal surface under investigation. Figure 7 shows a schematic of the method and a more detailed view of the actual apparatus.

The second method was based on two rotating slotted discs on a common axis with the second downstream disc rotationally displaced. The discs were displaced in such a way that only atoms transmitted by the slots of the first disc with the desired velocity could pass through the slots of the second disc. For the motor they modified a Gaede-Siegbahn molecular turbo pump which was already available at the time.² The 1 cm thick discs with the pump veins were replaced by two 12 cm dia 1 mm thick discs 3.1 cm apart each with 408 slits with a width of 0.4 mm.³ (Fig. 8).

²The molecular turbo pump was invented by Gaede in 1910; improved by Holweck in 1923 and by Manne Siegbahn in 1926.

³In the operation of the two disc velocity selector Stern and colleagues appear to have neglected the velocity side bands. For the transmitted velocity they assumed that only those atoms that passed a slit in the first disc could pass the next slit in the second disc-on the same axis-but displaced rotationally by one period with respect to the first disc. Thus the velocity is given by $v_0 = \ell \cdot v \cdot N$, where ℓ is the distance between discs, which is divided by the time for the disc to move by one slit, $\tau = 1/\nu N$,

Fig. 7 The apparatus used by Estermann, Frisch and Stern to measure diffraction of a velocity selected He atom beam [34]. **a** Schematic of the apparatus. By choosing the diffraction angle only atoms with the desired velocity are transmitted to the second crystal for diffraction. **b** Side view of the apparatus

Fig. 8 The second apparatus used by the same authors as in Fig. 7 to measure the diffraction of a velocity selected He atom beam [34]. **a** The velocity is selected by two rotating identical slotted discs, rotational displaced. **b** The sharp diffraction peaks made it possible to confirm the de Broglie wavelength within less than 1%

here ν is the frequency of rotations and N is the number of slits. But atoms with slower velocities will arrive at a later time when the second disc has rotated to the position of the second slit with velocity $v_1 = \frac{1}{2}v_0$ and be transmitted. Also very fast atoms that pass the slit in the second disc in the same position as in the first disc will be transmitted. For this reason, modern velocity selectors have several additional discs at strategic distances along the axis to block out the unwanted velocity side bands. The contribution of these side bands in the case of the Stern experiments is estimated by the author to amount to about 25%.

With the second apparatus Immanuel Estermann, Robert Frisch, and Otto Stern in No. 18 of the UzM series reported highly resolved diffraction patterns of monochromatized He atoms from LiF [34] (Fig. 8). In a footnote of the same UzM article they mention that in the initial measurements the experimental wavelength was smaller by 3% than the predicted wavelength. This, they were convinced, was far too large a discrepancy to be possible. After a long search it was ultimately found that the commercial precision graduated disc used by the Hamburg machine shop to locate the slots to be milled in the discs had 408 positions instead of the 400 specified by the supplier! When this was accounted for and after a careful calibration of the velocity selector and extensive measurements at different rotational frequencies and on different days they established that the diffraction angle was 19.45 deg corresponding to a de Broglie wave length $\lambda = 0.600 \times 10^{-8}$ cm. The de Broglie wavelength calculated for the transmitted velocity was 0.604×10^{-8} cm with a deviation of less than 1% from the measured value. This was the first precision measurement of the de Broglie wavelength of a massive particle. Otto Stern's strong conviction that something must be wrong with the initial results illustrates once more his extraordinary acumen as an experimentalist.

After 4 years, Otto Stern had finally achieved one of the goals that he had laid out when he came to Hamburg. In fact, Otto Stern, as it later became clear, was still not satisfied with these experiments. In an interview with Res Jost in Zürich in 1961 [37] Otto Stern began his comments with reference to the above experiments: *"I especially like this experiment, it is not properly recognized. It is about the determination of the de Broglie wavelength. All the parts of the experiment were classical except for the lattice constant. All the parts came out of the shop. The atom velocity was specified with pulsed slotted discs. Hitler is to blame that we could not end these experiments in Hamburg. It was on the list of projects to be done."* Here he implies that he had hoped to manufacture a regularly grooved grating in the shop as attempted in UZM, No. 11. Otto Stern would be happy to know that this experiment has recently been carried out in Berlin and is described in one of the following chapters by Wieland Schöllkopf.

In addition to the first observation of diffraction of massive particles and the confirmation of de Broglie's wave-particle duality, Otto Stern and his group made another important discovery. Already in the course of the first experiments, which led to clear diffraction peaks, Estermann and Stern in UzM No. 5 observed a series of four totally unexpected fairly sharp small minima upon azimuthal rotation of the target crystal [34]. They first considered that these could come from diffraction from unexpected structural modifications of the crystal. It was also speculated that they might be related to a layer of adsorbed molecules. To further investigate these anomalies, Frisch and Stern in UzM No. 23 constructed two new dedicated apparatus with additional degrees of freedom for moving the detector with respect to the crystal, but without velocity selection [35]. In one arrangement the diffraction angles could now be scanned out of the plane defined by the incoming beam and the crystal normal. In the other in-plane arrangement the incident angle could be varied and, in addition, the crystal could be rotated. In both arrangements, the distinct minima were confirmed and found to be even sharper. These they studied for He scattered from

Fig. 9 Anomalous dips in the diffraction pattern, observed by Frisch in 1933 [35]. Three years later Lennard-Jones and Devonshire showed that the dips were due to atoms temporarily bound on the surface in a process called Selective Adsorption [36]

LiF over a wide range of angles in both arrangements. Minima were also found for H_2 on LiF and also for He scattered from NaF (Fig. 9). In summarizing their 1933 experiments in UzM No. 23 they write that they could not come up with a completely satisfactory explanation of these minima. They also report that the process depends in a specific way on the incident direction and energy of the particles. In 1933 in UzM No. 25, one of the last articles from the Hamburg group, Frisch was the only author since Stern, when the paper was submitted, left Germany three days later and had been busy with preparing his exodus. In this article Frisch further summarizes and characterizes the experimental conditions under which the minima appeared [38]. Here he correctly (see below) concludes that the adsorbed atoms are trapped in the two dimensional periodic force field of the surface from which they are diffusely reemitted. Since the perpendicular component of the motion of the atoms bound to the surface in the potential well must be quantized the incident atoms must initially have a specific incident direction and energy in order to be trapped.

Three years later in 1936 the careful and complete documentation of the experimental conditions under which the minima occurred enabled Lennard-Jones and Devonshire to develop the correct theory. The special angles and velocities at which the anomalies occurred were explained by the conditions of resonant trapping of the atoms by diffraction into the bound states of the atom-surface potential [36]. According to their theory: *“Atoms moving along the surface with the right energy and in the right direction may be diffracted as to leave the surface with positive energy and thus be evaporated. This is a new mechanism of evaporation which has not been previously expected.”* Since the minima only occur at special angles they named the new phenomenon Selective Adsorption (SA).

Since their discovery in 1933 and the explanation by Lennard-Jones and Devonshire, selective adsorption resonances have been extensively studied [39]. Presently, they provide the most sensitive and most direct probe of the bound states of the atom-surface potential and thereby the best method for determining the atom-surface potential. Since SA involves diffraction, the surface must have a sufficient corrugation for the effect to occur. Results are presently available for a wide variety of corrugated insulator surfaces and also for metal surfaces with sufficient corrugation as in the case of higher-index stepped surfaces [40]. Since 1981 several new types of resonances involving resonant *inelastic* processes, in which the bound states play an important role, have been found [39]. After a discussion of the elastic selective adsorption resonances the different types of inelastic resonances will be discussed below.

5 The Present Day Legacy of Otto Stern's Surface Scattering Experiments

On June 23, 1933 Stern and his colleagues Estermann, Frisch and Schnurmann were notified that they were discharged from the University, only Knauer, who was not Jewish, could remain. Stern was fortunate to soon after obtain a research professorship at Carnegie Institute of Technology in Pittsburgh. There he continued his molecular beam experiments, but did not continue the He atom surface diffraction experiments.⁴ It appears that at the time he did not call attention or perhaps did not even realize the potential use of He atom diffraction for studying the structures of surfaces, which were largely unknown at the time. This we find surprising since in 1931 Thomas Johnson, who had reported diffraction of hydrogen atoms from LiF [42], wrote: "These experiments (diffraction of H₁, H₂ and He from LiF) are of interest not only because of their confirmation of the predictions of quantum mechanics, but also because they introduce the possibility of applying atom diffraction to investigations of the atomic constitution of surfaces. A beam of atomic hydrogen, ... has a range of wavelengths of the right magnitude ..., centering around 1 Å, and the complete absence of penetration of these waves will insure that the effects observed arise entirely from the outermost atomic layer".

Similarly, the significance and potential for surface physics of the 1927 electron scattering experiments of Davisson and Germer were not immediately realized. The experiments were only continued by Germer, who in 1929 reported on electron scattering to study gas adsorption [43]. Otherwise there were few immediate followers. One reason was that the apparatus used by Davisson and Germer were very fragile and prone to breakage. Also the preparation of metal surfaces was in the 1930s not well understood. Moreover, the depression in the 1930s and World War II halted

⁴In 1941, Bessey from the Carnegie Institute published a short note describing He and H₂ diffraction from LiF in which he thanks Otto Stern for suggesting the problem [41].

much of the fundamental research activities. One of the first to continue the experiments of Davisson and Germer was Harrison E. Farnsworth who was probably the first to use electron scattering to study the atomic structures of metal surfaces [44].

The remarkable experimental expertise of Otto Stern is well highlighted by the long time it took for others to repeat his He atom diffraction scattering experiments of 1929. The first post World War II attempt to repeat Stern's diffraction experiments was reported by J. Crews in 1962 [45] more than 30 years later. His angular distributions were not nearly as clearly resolved as in Stern's diffraction peaks. Also the 1968–1970 experiments of Okeefe et al [46, 47]. did not match up with the 1929 experiments. It was only after supersonic free jet expansion sources were introduced, with their inherent sharp velocity distributions, compared to the effusive atomic beam sources used by Stern, were comparable results achieved in 1973 [5]. Thus it took 44 years to arrive at a comparable technological-experimental level as achieved in the Hamburg group. This is even more surprising when it is realized that following the 1957 Sputnik shock the US embarked on a large program to compete scientifically with the Soviet Union. An important part of this program was to develop molecular beam research.

The outstanding experimental genius and foresight of Otto Stern was early on appreciated by the theoretician Max Born, who in 1919 had been Stern's colleague in Frankfurt. In his 1931 letter to the Nobel committee Born wrote: "According to my opinion Stern's achievement are far beyond those of other experimentalists through their conceptual boldness and also through the masterful overcoming of the experimental difficulties that I would like to propose no other physicist except him for the Nobel Prize."

The early history of atom and molecule surface scattering and diffraction experiments has been reviewed in the books by von Laue [48] and later in 1955 by Smith [49], and the more recent article by Comsa [50]. The first experimental studies of energy transfer in scattering from surfaces are described in the reviews by Beder [51], Stickney [52], and the author [53] and in 2018 in the monograph by Benedek and Toennies [39]. In 1969 Cabrera, Celli and Manson pointed out the possibility to observe single phonon excitations and their dispersion by inelastic diffraction of a He atom beam [53]. This stimulated several groups to carry out the corresponding scattering experiments. The first experiments to investigate the surface phonons of a crystal surface were performed by Brian Williams in Ottawa in 1971 [54]. He used essentially the same type of apparatus consisting of two diffraction surfaces that had been used by Estermann, Frisch and Stern for velocity selected diffraction in UzM No. 18. In the apparatus of Williams diffraction from the first crystal was used to select the velocity of the beam incident on the second crystal. The diffraction from the second crystal served to detect the inelastic change in velocity. Through an ingenious use of special kinematic conditions at certain incident and/or final directions additional small peaks in the angular distributions gave the first information on surface phonons on LiF(001) [54, 55]. Soon after in 1974 Boato and Cantini [56] also used high resolution angular distributions to study surface phonons with helium and neon scattered from LiF(001). Several groups also used time-of-flight inelastic scattering in further attempts to investigate the phonons on the surfaces of LiF [57] and on metals [58].

The first He atom inelastic time-of-flight experiments which were able to fully resolve single phonons and allowed the measurement of the dispersion curves of surface phonons out to the zone boundary were reported in 1981 by Brusdelylins, Doak and Toennies for the LiF surface [59] and in 1983 for a metal surface [60]. Similar measurements on metals using inelastic electron energy loss (EELS) were successfully carried out at about the same time [61, 62]. The He atom experiments were facilitated by the 1977 discovery that at high expansion pressures of about 100 bar free jet expansions of He have an inherent sharp velocity distribution corresponding to $\Delta v/v \approx 10^{-2}$ [63]. It was no longer necessary to use diffraction and rotating discs to select the beam velocity.

The above experiments, continuing on the footsteps of Otto Stern, have established He atom scattering as a unique and indispensable surface science tool. A beam of He atoms in the thermal energy range (5–100 meV) is completely non-penetrating, chemically inert and produces no mechanical damage. Because of its matter-wave property it is the ideal method to project out of the chaotic vibrating surface by inelastic diffraction the phonon dispersion curves. Electron beams have also this property but since the electrons at the same wave length have much higher energies the electrons penetrate the surface and can damage the crystal. The modern experiments in which He atom diffraction is used to study the surface structures of insulating, semiconductor and metal surfaces have been reviewed by Rieder and Engel [64] and by Farias and Rieder [65]. The Helium Atom Scattering (HAS) studies of the phonon dispersion curves of clean surfaces and the vibrations of adsorbate-covered surfaces have very recently been surveyed in the 2018 book by Giorgio Benedek and J. P. Toennies entitled “Atomic Scale Dynamics at Surfaces: Theory and Experimental Studies with Helium Atom Scattering” [39]. There also the very recent understanding that He atoms interact with the electron densities at the surface and provide detailed information on the electron-phonon coupling constant is discussed.

6 New Applications of Matter-Wave Diffraction from Manufactured Nanoscopic Gratings

The advent of nanotechnology in the last 30–40 years has opened up new opportunities to utilize the wave-particle duality for investigations of the physical properties of atoms, molecules and clusters. Some very recent developments in this area are covered in the review articles in this book following this introductory historical review. Here only some early pioneering experiments are dealt with.

Free standing transmission gratings with a slit spacing commensurate with wave lengths in the soft X-ray and the extreme ultraviolet regime, where traditional optical elements are opaque, were first developed for spectroscopy. With decreasing structural dimensions, nanostructured transmission gratings have made it possible to carry over to massive particles with much smaller wave lengths the interference phenomena which had been exploited for light.

Keith, Schattenburg, Smith and Pritchard at MIT were the first in 1988 to report the diffraction of atoms from a fabricated transmission grating [66]. In their experiment Na atoms from an in Ar seeded beam with a de Broglie wave length of 0.017 nm (0.17 Å) were diffracted by an angle of about 70 μ rad with an angular resolution of 25 μ rad(!) after passing through a specially fabricated 0.2 μ m period gold grating with slits and bars of 0.1 μ m width. Previously, the same group had also shown that atoms could be diffracted from a standing wave of near resonant light [67]. Subsequently, in 1991, Carnal and Mlynek demonstrated a simple interferometer based on Young's double slit experiment using 2 μ m wide slits [68]. Since these initial experiments transmission grating diffraction has been reported for molecules such as Na₂ [69], C₆₀ [70, 71], C₆₀F₄₈ and C₄₄H₃₀N₄ and also for small helium clusters [72–74], with up to about 50 atoms [74–76].

The author's group in 1994 applied transmission grating diffraction as a type of mass spectrometer to establish the existence of the He atom dimer [72, 73]. The existence of the He dimer was long questioned since the long range attractive potential could not be predicted with sufficient accuracy to establish if the very weak attraction between the atoms would be strong enough to support a bound state. A 1993 claim based on mass spectrometer detection [77] was subsequently questioned [78, 79]. Figure 10 shows the diffraction apparatus used by our group [80]. The mass selection comes about since the de Broglie wave length and the diffraction angle are inversely proportional to the mass of the diffracted particles. Since only wavelets which pass through the slits coherently without any interaction with the grating bars can contribute to the diffraction peaks this type of mass spectrometer is completely non-destructive.

Figure 11 displays some diffraction patterns taken at different source temperatures and a high resolution measurement showing well resolved dimer and trimer

Fig. 10 The transmission grating diffraction apparatus used by the author's group to detect the helium dimer and other small He clusters [80]

Fig. 11 **a** He atom diffraction patterns measured at three different decreasing source temperatures with increasingly large de Broglie wavelengths. At the lowest temperature between the central specular peak and the first order atom diffraction peaks at -4 and $+4$ degrees additional diffraction peaks appear which correspond to the dimer, trimer and tetramer of helium. **b** The same diffraction peaks measured with a much increased angular resolution [81]

first order diffraction peaks. The sharp velocity distributions of high-pressure free jet expansions of helium [63], which is also found for the clusters of helium, greatly facilitated the resolution of the diffraction experiments. The partly resolved anomalies in the diffraction patterns of larger helium clusters with up to 50 atoms revealed unexpected maxima and minima instead of a broad peak expected for liquid clusters. The corresponding magic numbers provided the first evidence for the quantum levels of these small superfluid clusters [74].

It was even possible to measure the size of the He-dimer from the intensity distribution of the diffraction peaks [82]. The weak bond of the dimer makes it sensitive to even the slightest interaction with the grating bars. Depending on the size of the dimer the effective slit and coherence width are reduced accordingly. The effective width was experimentally determined from the *slit function* which is the envelope over all the diffraction peaks out to high order. From extensive measurements of the diffraction patterns of the He atom and He dimer it was found that the dimer diffraction

Fig. 12 **a** The probability amplitude of the He dimer which is compatible with the measured mean radius of the dimer of 5.2 ± 0.4 nm [82]. **b** An expanded view of the potential showing that the highly quantum dimer tunnels far beyond the classical outer turning point located at about 1.4 nm

peaks were associated with a significantly smaller slit width, which corresponds to a larger size, than that of the atoms. With the aid of a many-body quantum scattering theory the difference in slit width could be referred to the mean internuclear distance of the dimer $\langle R \rangle$ [83]. The extreme sensitivity is illustrated by the fact that $\langle R \rangle$ was found to be 5.2 ± 0.4 nm. The uncertainty was only 0.4% when compared to the 100 nm overall slit width of the grating.⁵ This experiment established that the dimer is the largest of all ground state molecules and is about 70 times larger than the H_2 molecule (Fig. 12). It also provided the first measurement of the dimer van der Waals bond which is still an important benchmark for quantum chemists. From the bond distance the binding energy was calculated to be only $96^{+26}_{-17} \times 10^{-9}$ eV ($1.1^{+0.3}_{-0.2}$ mK) [82] which corresponds to a scattering length of about $s = 100$ Å.

In the case of other atoms and tightly bound molecules the effective slit and coherence width depend on the long range van der Waals interaction with the solid surface given by $V(l) = -C_3/l^3$, where l is the distance of the particle from the slit surface as it passes through the slits of the grating. Both the magnitude of the corresponding reduction in the effective slit width and its velocity dependence were fitted with a scattering theory to provide values of the van der Waals constant C_3 [84]. The values obtained showed the expected linear increase of C_3 with the polarizability of the particle increasing in the order of He, Ne, D_2 , Ar und Kr. These experiments represent the first quantitative measurements of C_3 . The method was subsequently used to determine the C_3 constants of the alkali atoms [85, 86] and of metastable atoms [87] and to set limits on the strength of the non-Newtonian gravity at short length scales [86].

⁵The method is so sensitive that the effect of a monolayer of adsorbed Xe in narrowing the slit width by about 7 Å could be measured by comparing the slit width with a cold and a hot grating in the presence of ambient Xe[(unpublished)].

Quite recently, the non-destructive selection of small helium clusters by diffraction from a transmission gratings has facilitated a remarkable study. In this experiment the actual radial distribution function of the neutral atoms in the dimer could be measured from the distribution of the helium ions released in the femtosecond laser induced Coulomb explosion [88]. The experimental distribution confirmed the large size of the dimer and revealed that it extended out to distances of more than 23 nm far beyond the classical outer turning point at 1.4 nm [88]. From the exponential fall-off of the radial distribution the binding energy was determined to be $151.9 \pm 13.3 \times 10^{-9}$ eV (1.5 ± 0.13 mK) with the highest precision so far. With the same apparatus in another remarkable experiment the radial distributions of the three helium atoms in the first excited Efimov state of helium trimer could also be measured [89]. This is the first direct measurement of the size of an Efimov state. This unique quantum state was already predicted by Efimov in 1970 to occur for three bosons, of which each of the pairs are critically bound with a nearly vanishing binding energy [90]. As a result of the smaller binding energy the radial distribution of the Efimov trimer extends to even larger distances than in the dimer making the trimer even larger in size than the C_{60} molecule and many biological molecules and even viruses.

The de Broglie wavelength of atoms has also been the basis of using transmission Fresnel zone plates for focusing atomic beams. The focusing via Fresnel zone plates with many concentric slits was first demonstrated by Carnel et al. already in 1991 [68]. Using easily detected electronically excited He atoms they were able to focus down to a spot size of 15–20 μm with an intensity of 0.5 counts/s. In 1999, Doak et al. from our laboratory using a miniature 0.27 mm overall dia. zone plate with a smallest outermost slit width of 100 nm (this is also the predicted diffraction limited resolution) achieved with neutral He atoms a 2 μm dia spot with an intensity of 350 counts/s [91]. Recently, the spot size was reduced down to 1 μm but with an intensity of only 125 counts/s [92].

The first interferometers based on matter wave diffraction were with electrons [93–95] and neutrons [96, 97]. In both experiments the passage through a well-ordered crystal was used as the diffracting element. A Mach-Zehnder interferometer using transmission gratings with Na atoms was first reported by Keith et al. [98]. Subsequently, the same interferometer was used to demonstrate the loss of coherence by scattering photons from one of the paths through the interferometer [67]. Since these seminal demonstration experiments interferometry with atoms has become a wide field of activity stimulated by advances in laser and nanotechnology and laser cooling techniques [99, 100]. The recent advances are the subject of the article by Stefan Gerlich and colleagues in the next chapter.

The construction of a simple robust and compact three grating Mach-Zehnder interferometer developed in our group is shown in Fig. 13 [101]. A homogeneous electric field in one of the interfering arms was used to shift the phase in one of the two separate branches with respect to the other branch. Figure 14 shows the resulting interference fringes. In this experiment a novel extremely accurate lower limit on the velocity half-width of a He atom free jet beam could be demonstrated. In one branch of the interferometer an electric field was applied. With increasing field strength one half of the beam was shifted in phase with respect to the beam without an applied

Fig. 13 **a** Schematic diagram of the compact Mach-Zehnder Interferometer constructed by the Göttingen group. **b** Perspective view of the interferometer showing the piezos to adjust the gratings and the magnetic vibration stabilization to reduce the vibrations to less than 1×10^{-6} m [101]

field. The interference pattern of Fig. 14 shows the interferences as one half of the cold 6 K beam with a de Broglie wave length of 0.4 nm ($4 \text{ \AA}$) had been shifted with respect to the other half by 25 wave lengths. The largest shift corresponds to a lower limit on the parallel coherence length of $25 \times 4 \text{ \AA} = 100 \text{ \AA}$, which corresponds to a velocity half width of only 10 m/sec.

A Mach-Zehnder interferometer also provides a precise method for measuring polarizabilities as was demonstrated for the highly polarizable sodium [102] and lithium [103]. Figure 15 shows the results of an interferometer experiment designed to measure the polarizability of the weakly bound He dimer. In the diffraction pattern at the outlet of the interferometer diffraction peaks due to the dimer could be identified between the more intense peaks of the He atom component. From the phase

Fig. 14 Interference fringes obtained with a free jet expanded He atom beam with a de Broglie wavelength of 4 Å [101]

Fig. 15 The polarizability of the He dimer is measured in the same arrangement as Figs. 13 and 14 [101].

a From the diffraction pattern at the output of the interferometer, a small dimer peak could be identified at -1.4 mrad. **b** From the interference fringes measured at this angle with increasing voltage the polarizability of the He dimer was found to be somewhat smaller than that of two separate atoms

shift with voltage the polarizability of both the He atom and the dimer could be measured relative to each other. Since the atom polarizability is well-known from both metrological experiments and from theory the polarizability of the He dimer could be calibrated by comparison with the He atom beam component and found to be

$$\propto (\text{He}_2) = 0.30884 \pm 0.001883 \text{ \AA}^3,$$

which is to be compared with the polarizability of two He atoms:

$$\propto (2\text{He}) = 0.3113 \pm 0.0023 \text{ \AA}^3.$$

The smaller polarizability of the dimer is expected since the electrons in the dimer are very slightly more bound than in the fully separated atoms. This preliminary result serves to illustrate the remarkable sensitivity of the method. In a similar manner the comparatively large polarizabilities have been measured of the alkali atoms Li [104] and Na, K, and Rb [105].

7 Summary

In the 90 years since Otto Stern had demonstrated that wave-particle duality also applied to massive particles, the wave nature of atoms and molecules has found widespread applications in both physics and chemistry. The first experiments of He atom diffraction scattering from LiF crystals by Otto Stern in 1929 have since evolved into a gentle nondestructive and universal tool for the determination of the structure of clean and adsorbate-covered surfaces and for the measurement of the phonon dispersion curves at the surfaces of a wide range of different types of solids [39]. In the latter application, He atom scattering is the ideal complement to the scattering of neutrons, which since they pass through the crystal virtually unhindered, are only sensitive to the bulk phonons.

Since Otto Stern's days new nanotechnology advances have opened up an entire new field of experiments based on matter wave behavior of atoms and molecules. As discussed here these encompass on the one hand the non-destructive mass analysis of fragile clusters and on the other hand the precision interferometry of atomic and molecular properties. Certainly, Stern would have been happy to learn about the many wonderful and important applications of matter waves of atoms and molecules discussed here and described in the following chapters.

In this connection, the author, after having been occupied with the impact of Otto Stern's 1929 diffraction experiments, often wonders whether Stern at the time realized the many future important applications arising out of his pioneering experiments. It is interesting that he had attempted and had hoped to carry out diffraction experiments from man-made ruled gratings, only recently realized and described by Wieland Schöllkopf in the following chapter.

Otto Stern was definitely very much aware of the fundamental importance of his experiments in relation to the electron diffraction experiments and the implications for quantum theory as expressed in his 1943 Nobel lecture: “*With respect to the differences between the experiments with electrons and molecular rays, one can say that the molecular ray experiments go farther. Also the mass of the moving particle is varied (He, H₂). But the main point is again that we work in such a direct primitive manner with neutral particles. These experiments demonstrate clearly and directly the fundamental fact of the dual nature of rays of matter. It is no accident that in the development of the theory the molecular ray experiments played an important role. Not only the actual experiments were used, but also molecular ray experiments carried out only in thought. Bohr, Heisenberg, and Pauli used them in making clear their points on this direct simple example of an experiment...*” Here Otto Stern calls attention to the important impact of de Broglie’s theory and his experiments on the development of quantum theory especially by Erwin Schrödinger. To do justice this aspect would be beyond the scope of this article.

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