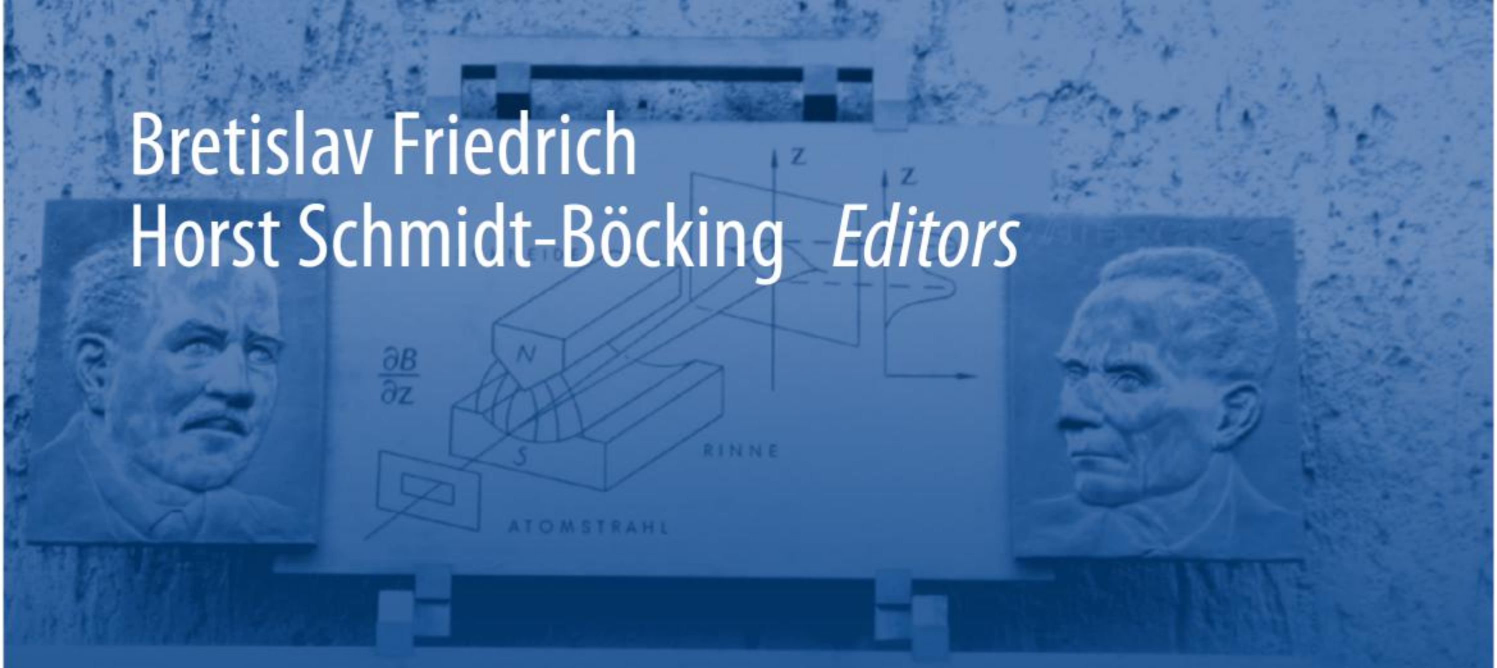
Bretislav Friedrich
Horst Schmidt-Böcking *Editors*



Molecular Beams in Physics and Chemistry

From Otto Stern's Pioneering Exploits to Present-Day Feats

OPEN ACCESS

Springer

Molecular Beams in Physics and Chemistry

Bretislav Friedrich · Horst Schmidt-Böcking
Editors

Molecular Beams in Physics and Chemistry

From Otto Stern's Pioneering Exploits to Present-Day Feats

Springer

Editors
Bretislav Friedrich
Fritz-Haber-Institut der
Max-Planck-Gesellschaft
Berlin, Germany

Horst Schmidt-Böcking
Institut für Kernphysik
Universität Frankfurt
Frankfurt am Main, Hessen, Germany

ISBN 978-3-030-63962-4 ISBN 978-3-030-63963-1 (eBook)
https://doi.org/10.1007/978-3-030-63963-1

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Chapter 25
Grating Diffraction of Molecular Beams: Present Day Implementations of Otto Stern's Concept

Wieland Schöllkopf

Abstract When Otto Stern embarked on molecular-beam experiments in his new lab at Hamburg University a century ago, one of his interests was to demonstrate the wave-nature of atoms and molecules that had been predicted shortly before by Louis de Broglie. As the effects of diffraction and interference provide conclusive evidence for wave-type behavior, Otto Stern and his coworkers conceived two *matter-wave* diffraction experiments employing their innovative molecular-beam method. The first concept assumed the molecular ray to coherently scatter off a plane ruled grating at grazing incidence conditions, while the second one was based on the coherent scattering from a cleaved crystal surface. The latter concept allowed Stern and his associates to demonstrate the wave behavior of atoms and molecules and to validate de Broglie's formula. The former experiment, however, fell short of providing evidence for diffraction of matter waves. It was not until 2007 that the grating diffraction experiment was retried with a modern molecular-beam apparatus. Fully resolved matter-wave diffraction patterns were observed, confirming the viability of Otto Stern's experimental concept. The correct explanation of the experiment accounts for *quantum reflection*, another wave effect incompatible with the particle picture, which was not foreseen by Stern and his contemporaries.

1 Introduction

The time when Otto Stern and his coworkers at the University of Hamburg were running their pioneering molecular-beam experiments almost a century ago, saw disruptive breakthroughs in quantum physics, experimental and theoretical alike. Among the latter was arguably the work of the french physicist Louis de Broglie on the wave nature of massive particles [1]. He came forward with a rather simple formula for the wavelength λ_{dB} of a *matter wave*, predicting that it equals the product

W. Schöllkopf (✉)
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
e-mail: wschoell@fhi-berlin.mpg.de

B. Friedrich and H. Schmidt-Böcking (eds.), *Molecular Beams in Physics and Chemistry*,
https://doi.org/10.1007/978-3-030-63963-1_25

of Heisenberg's constant h and the inverse of the classical momentum $p = mv$ of a particle of mass m and velocity v.

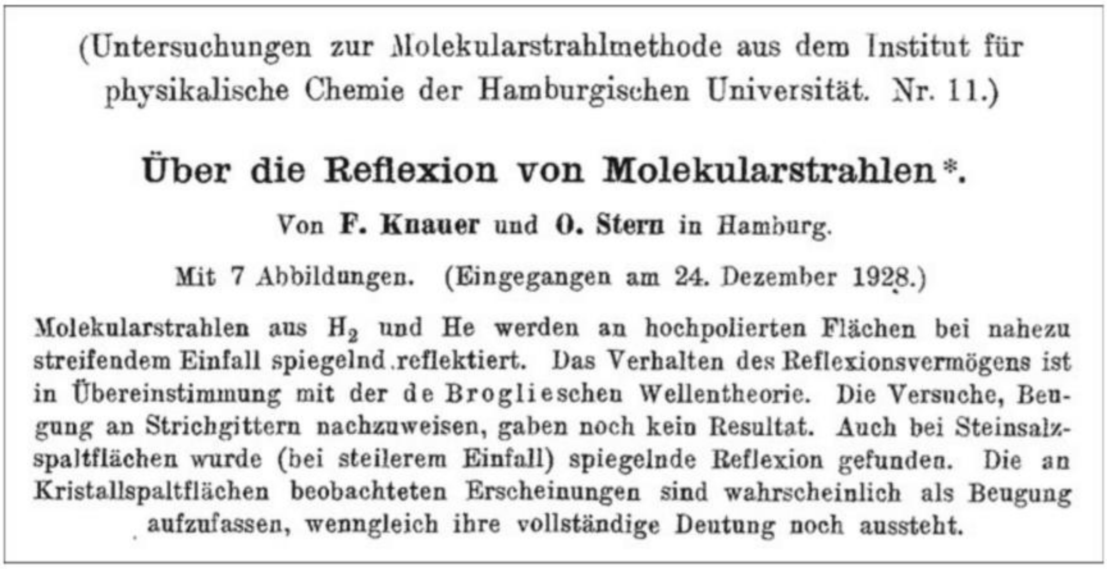
$$\lambda_{\mathrm{dB}} = \frac{h}{mv} \tag{1}$$

Given the boldness of the concept of matter waves combined with the simplicity of de Broglie's formula it is not surprising that experimentalists—and a theorist-turned experimentalist such as Otto Stern in particular—must have felt challenged to seek experimental evidence for the existence of de Broglie's matter waves.

Diffraction and interference are unambiguous manifestation of wave-type behavior. As such, Otto Stern and his coworkers conceived two matter-wave diffraction experiments employing their molecular beam method. They had to cope with the fact that, according to Eq. (1), a typical de Broglie wavelength, even for lightweight atoms, at room temperature conditions is in the sub-nanometer regime. Observation of diffraction effects for a wavelength that small requires diffractive optical elements, such as gratings or grids, of a similarly small periodicity. In their article UzM[1] no. 11 *Über die Reflexion von Molekularstrahlen* (Fig. 1) that appeared in Zeitschrift für Physik in 1929 [2] Friedrich Knauer and Otto Stern outlined the two methods they considered promising and they pursued for observing diffraction of a molecular beam. The first one assumes the atoms or molecules to scatter off of a plane ruled (machined) grating at grazing incidence conditions, while the second one was based on the scattering from a cleaved crystal surface.

The latter method was essentially analogous to X-ray diffraction from a crystal lattice, a phenomenon already well known by the mid 1920s. Its first observation by Max von Laue, Walter Friedrich, and Paul Knipping in 1912 provided conclusive evidence for both the wave nature of X-rays and the periodic structure of a crystal lattice (for an historical account on von Laue's experiment see Ref. [3]). X-ray wavelengths are of the same order of magnitude as typical de Broglie wavelengths of light atoms at thermal energies. Crystal lattices, with sub-nanometer periodicity, present a natural match to these wavelengths resulting in comparatively large diffraction angles. Obviously, the main difference is that molecular beams, unlike X-rays, cannot penetrate a crystal. Thus, Otto Stern's approach relies on reflection of a molecular beam from a cleaved crystal surface, which needs to be clean and well-ordered on the atomic scale to allow for coherent scattering of atoms or molecules. While Knauer and Stern where able to observe specular reflection from a crystal surface, they could not present convincing evidence for diffraction of the molecular beam by the periodic crystal lattice. It was several months later, after some improvement of the experimental setup, that Otto Stern together with Immanuel Estermann was able to present unambiguous evidence for diffraction [4]. This work from Otto Stern's molecular beam lab provided the first definite evidence for matter-wave behavior of

[1]UzM stands for *Untersuchungen zur Molekularstrahlmethode*, the series of publications from Stern's molecular-beam lab in Hamburg termed *Investigations by the Molecular Ray Method*, c.f. *Otto Stern's Molecular Beam Method and its Impact on Quantum Physics* by Bretislav Friedrich and Horst Schmidt-Böcking in this volume.



(Untersuchungen zur Molekularstrahlmethode aus dem Institut für physikalische Chemie der Hamburgischen Universität. Nr. 11.)

Über die Reflexion von Molekularstrahlen*.

Von **F. Knauer** und **O. Stern** in Hamburg.

Mit 7 Abbildungen. (Eingegangen am 24. Dezember 1928.)

Molekularstrahlen aus H_2 und He werden an hochpolierten Flächen bei nahezu streifendem Einfall spiegelnd reflektiert. Das Verhalten des Reflexionsvermögens ist in Übereinstimmung mit der de Broglieschen Wellentheorie. Die Versuche, Beugung an Strichgittern nachzuweisen, gaben noch kein Resultat. Auch bei Steinsalzspaltflächen wurde (bei steilerem Einfall) spiegelnde Reflexion gefunden. Die an Kristallspaltflächen beobachteten Erscheinungen sind wahrscheinlich als Beugung aufzufassen, wenngleich ihre vollständige Deutung noch aussteht.

Fig. 1 Front page of the UzM paper no. 11 "*On the reflection of molecular beams*" by Friedrich Knauer and Otto Stern as it appeared in Zeitschrift für Physik in 1929 (received by the journal on December 24, 1928) [2]. In English the abstract states: *Molecular beams of H_2 und He are specularly reflected from highly polished surfaces under near grazing incidence. The reflectivity behavior is in agreement with de Broglie's wave theory. Attempts to find evidence for diffraction from a ruled grating have not yet yielded results. For cleaved surfaces of rock salt (at steeper incidence) reflection was found as well. The phenomena observed with cleaved crystal surfaces are likely due to diffraction, albeit a complete interpretation is still missing*

atoms and molecules. In addition, Estermann and Stern were able to quantitatively check and validate Louis de Broglie's wavelength formula, Eq. (1), for atoms and molecules [4–6].

The success of Knauer's and Stern's second method leaves us with the question: What about the first concept they had conceived to demonstrate matter-wave diffraction with molecular beams; diffraction of a molecular beam reflected from a machined line grating under grazing incidence conditions? The remainder of this contribution will focus on this experiment. In Chap. 2 we will review how Knauer and Stern designed and implemented the grating diffraction experiment and see what results they got with their 1928 molecular beam apparatus. In Chap. 3 we will describe the modern implementation of the experiment, and we will discuss the explanation of the results accounting for quantum reflection. Quantum reflection from the attractive long-range branch of the atom–surface interaction potential is another quantum-wave phenomenon which is incompatible with a particle description. Quantum reflection was not foreseen by 1928, although it is a direct consequence of and evidence for quantum-wave behavior just as diffraction is.

2 The Grating Diffraction Experiment by Knauer and Stern in 1928

In the first paragraph of the UzM no. 11 article Knauer and Stern describe their considerations regarding the two experimental methods they are pursuing with the aim to observe matter-wave diffraction. The original German text reads:

> Der Nachweis der Wellennatur schien uns am bequemsten mit einem Gitter zu führen zu sein. Am nächsten läge es, an die bei den Röntgenstrahlen mit so großem Erfolg benutzten Kristallgitter zu denken. Doch ist von vornherein schwer zu übersehen, ob hier Reflexion und Beugung auftreten werden, weil es im Gegensatz zu den Röntgenstrahlen bei den de Broglie-Wellen auf den Potentialverlauf an der äußeren Grenze der Kristalloberfläche ankommt. Wir beabsichtigen deshalb, optische Strichgitter zu benutzen. Hierfür ist die Voraussetzung, dass es zunächst gelingt, Molekularstrahlen spiegelnd zu reflektieren.

For convenience we are here providing an English translation to the unfortunate reader who is not proficient in German.

> Providing evidence of the wave nature appeared to be most straightforward by using a grating. The most obvious choice would be a crystal lattice which has been used to great success with X-rays. It is, however, difficult to predict if reflection and diffraction will occur, because for de Broglie waves, in contrast to X-rays, the shape of the interaction potential at the outer limit of the crystal surface matters. That is why we intend to use optical ruled gratings. It is prerequisite to first succeed in observing specular reflection of molecular beams.

Apparently, Knauer and Stern were not sure if and to what extent the interaction potential that an atom is exposed to at a crystal surface would possibly impede the observation of diffraction. Therefore, they intended to (also) employ optical ruled gratings in their quest for matter-wave diffraction. For this approach to work it is prerequisite to achieve mirror-like (specular) reflection.

In the following lines Knauer and Stern describe why grazing incidence represents a pivotal aspect of the experimental design. Firstly, the grazing incidence geometry allows for the use of a large (macroscopic) grating period length in the range of 0.01–0.1 mm to diffract wavelengths as small as 0.1 nm. At grazing incidence the effective period that determines the diffraction angles is given by the projection of the grating period along the direction of motion of the incoming molecular beam. Thus, for a grazing angle of 1 mrad the effective period of a 10-micron-period grating is as small as 10 nm. While this is still roughly a factor of 100 larger than the de Broglie wavelengths we are dealing with, it results in diffraction angles of several milliradian, which are well within the experimental resolution. Secondly, the surface roughness, which Knauer and Stern estimate to be on the order of 10–100 nm for their well polished surfaces, would prevent mirror-like reflection at steep incidence. However, as it is known from optics, even a rough surface becomes highly reflective at grazing incidence conditions. Knauer and Stern assume that the roughness times the sine of the incidence angle needs to be smaller than the de Broglie wavelengths if one wants to get good reflectivity. That is why they expect mirror-like reflection of molecular beams from their surfaces for milliradian incidence angles. Interestingly, in this consideration Knauer and Stern ignore a possible influence of the atom-surface interaction potential on the reflectivity.

2.1 Apparatus

The apparatus used by Knauer and Stern was already described in some detail in the preceding paper UzM no. 10 [7], which appeared back to back with their UzM no. 11 paper in volume 53 of Zeitschrift für Physik in 1929. The apparatus allowed them to generate molecular beams of various gases including He, H_2, Ne, Ar, CO_2. As can be seen in the original schematics replotted in Fig. 2, the main components included (i) the molecular beam source, (ii) the detector, (iii) the 3-slits beam collimation system, and (iv) the encasing vacuum system. It appears that all four components were state-of-the-art at that time representing significant improvements compared to previously used molecular beam setups.

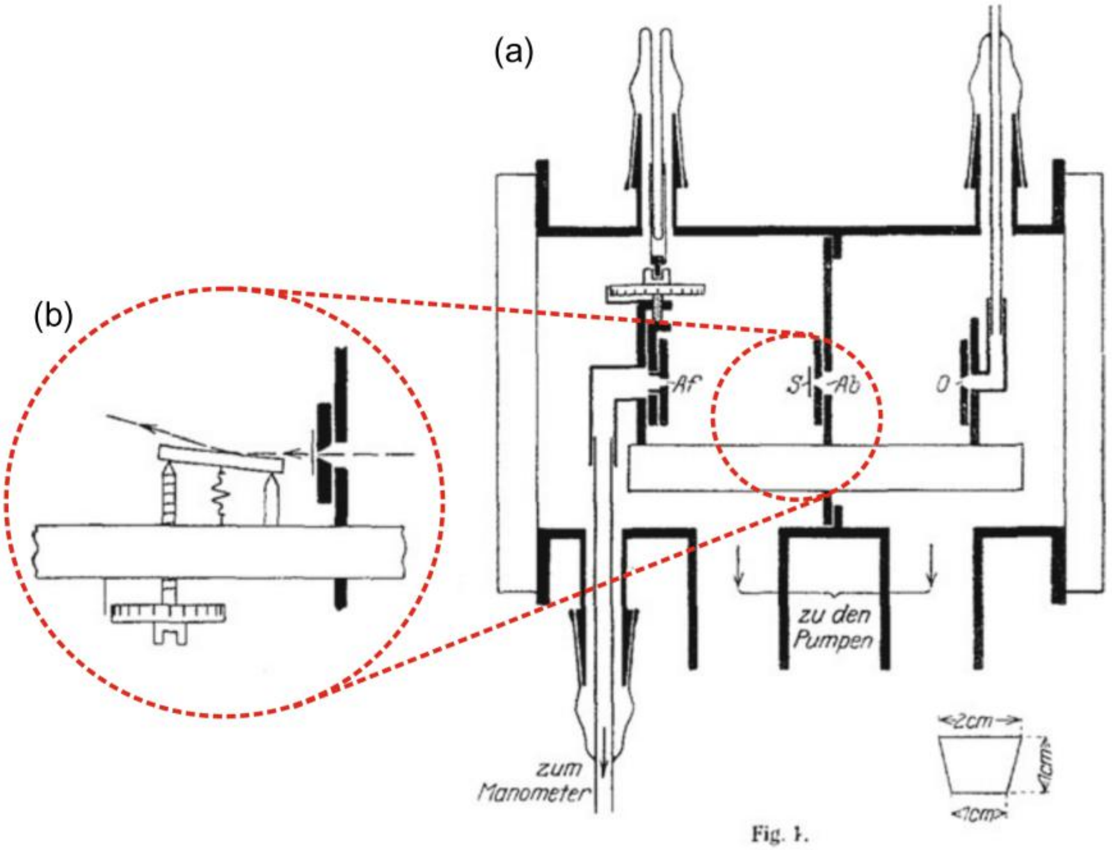


Fig. 2 Schematic of the experimental arrangement used by Knauer and Stern in 1928 copied from the original articles UzM no. 10 and 11. The dashed red circles indicate where the diffraction grating shown in the enlargement (**b**) (from Ref. [2]) was mounted in the molecular-beam apparatus shown in (**a**) (from Ref. [7]). The drawing in the lower right shows the trapezoidal cross section of the horizontal precision nickel-steel rod carrying the slits and the grating mount. The labels *Af*, *Ab*, and *O* denote the three collimating slits; *Auffängerspalt* (collector slit), *Abbildespalt* (imaging slit), and *Ofenspalt* (oven slit i.e. source slit). A shutter (*S*) is located downstream of the imaging slit. As described in the original text, a fourth slit *Vorspalt* (ante slit), not shown in the figure, was used in the grating diffraction experiments. It was located in between *O* and *Ab* and served as a differential pumping stage upstream of *Ab*

Molecular beam source: The gas was fed into a beam source from which it escaped through a narrow slit (10 to 20 μm wide) into the surrounding vacuum chamber. In today's jargon the source would be referred to as an effusive source, where the molecular beam inherits its velocity distribution from the Maxwell-Boltzmann distribution of the gas upstream the slit. Thus, unlike the supersonic free-jet expansion sources that have been available for the last few decades with their inherently narrow velocity distribution, the beams of Knauer and Stern were characterised by relatively large velocity spreads. This, via Eq. (1), corresponds to a wide distribution of de Broglie wavelengths. In other words, Knauer's and Stern's source did not generate monochromatic matter waves. Nonetheless, they were able to adjust the mean velocity and hence the mean de Broglie wavelength by as much as 50% by heating the source or by cooling it down to about 130 K.

Beam collimation and vacuum system: As in classical optics, matter-wave diffraction can only be observed, if spatial coherence is achieved in the experimental setup. This is done by three collimating slits: the first one defines the source (source slit described above); the second one limits the divergence of the beam; and the third one defines the angular resolution of the detector (detector slit described below). All three slits were 10–20 μm wide and 1 cm in height. From the schematic shown in Fig. 2b it can be seen that the second slit also served to effectively separate the vacuum of the right source chamber from the left beam chamber. The chambers were evacuated to a base vacuum pressure of 10^{-5} Torr by two mercury diffusion pumps made by Leybold [7].

Detector: In the Stern Gerlach experiment a few years earlier detection of the beam of silver atoms was accomplished by depositing the beam on a glass plate. After running the experiment for some time, one would check the thickness and location of the deposits. While this method allowed for the detection of the famous two-spot pattern in the Stern Gerlach experiment, it did not enable reliable quantitative measurements of beam intensities, not to mention the fact that the technique did not work with molecular beams of gases. Knauer's and Stern's detector, which is described in the UzM paper no. 10 [7], represents an enormous improvement. Their detector is essentially a Pitot tube with a narrow entrance slit (10–20 μm wide, just as the source slit). The stagnation pressure building up in the detector is measured by a modified Pirani-type vacuum gauge that Knauer and Stern were running at liquid nitrogen temperature. They were able to achieve an impressive absolute sensitivity on the order of 10^{-8} Torr [7]. With the base vacuum pressure in the 10^{-5} Torr regime, this translates into a relative sensitivity of 10^{-3} providing the required sensitivity for the diffraction experiment.

The optical elements—mirrors and gratings: Knauer and Stern were employing different materials for the mirrors they used in the reflectivity measurements: glass, steel, and speculum metal. The text states that each mirror was most thoroughly polished. The ruled gratings they employed in the diffraction experiments were all made from speculum metal with different periods of 10, 20 and 40 μm. No information is provided on how the ruling of the grating was done or what the groove shape might have been.

2.2 Results

Knauer and Stern observed specular reflection of He and H_2 beams from flat solid surfaces made out of any of the three materials. They found the reflectivity to slightly decrease from speculum metal to glass to steel, an observation they explained as a result of the somewhat different surface qualities achievable by polishing these materials. In addition, for each mirror they observed a strong decrease of reflectivity with increasing incidence angle. As an example they provide a reflectivity table for a beam of H_2 reflected from a speculum metal mirror including four data points decreasing from 5% at an incidence angle of 1 mrad to 0.75% at 2.25 mrad. Furthermore, they were able to increase the mean de Broglie wavelength of the molecular beam by cooling the beam source to $-150\,^{\circ}$C. They state that the observed reflectivity increased by a factor of 1.5 when the mean de Broglie wavelength of the molecular beam was increased by 1.5.

Despite the promising observation of mirror-like specular reflection of the molecular beam it was not possible for Knauer and Stern to observe diffraction when they were employing ruled gratings made out of speculum metal. They searched for diffraction signal in the incidence angle range from 0.5 to 3 mrad, but did not find reliable evidence:

> Wiewohl wir mehrmals Andeutungen eines Maximums gefunden zu haben glauben, gelang es uns nicht, sein Vorhandensein sicherzustellen.

> Although we believe to have seen hints of a [diffraction] peak several times, we were not able to verify its occurrence.

They make this clear in the article's abstract where they summarise *Die Versuche, Beugung an Strichgittern nachzuweisen, gaben noch kein Resultat*, which translates to English as *Attempts to find evidence for diffraction from a ruled grating have not yet yielded results*.

Apparently, Otto Stern planned to try matter-wave diffraction from ruled gratings again with an improved apparatus. As it is described on page 782 of UzM no. 11, a pump of "extremely high pumping speed" was already under construction for Stern's lab at the Leybold company. Stern hoped that the more powerful pump could further boost the molecular beam intensity. We do not know if this apparatus upgrade was implemented. By the time Stern had to leave Hamburg, diffraction from a ruled grating had not been observed in his lab. It would have been described, for instance, in the chapter that Robert Frisch and Otto Stern contributed to the Handbuch der Physik in 1933 [6]. In Peter Toennies's contribution *Otto Stern and Wave-Particle Duality* in this volume the reader will find an account of an interview Otto Stern gave in 1961, where he emphasised his interest in the grating diffraction experiment. As we will see in Sect. 3, Otto Stern's experimental approach was conceptually perfectly viable.

2.3 Historical Note on Friedrich Knauer

From a historical point of view it is intriguing to have a look at Friedrich Knauer, Otto Stern's assistant and only coauthor of the article UzM no. 11 on reflection from ruled gratings. The following basic biographical information is available at Knauer's *Wikipedia* entry: Born in Göttingen in 1897, Knauer studied in Göttingen and Hannover after the First Wold War. He was assistant to Robert Wichard Pohl in Göttingen in 1924, when he moved to Hamburg, where he worked as an associate of Otto Stern's until Stern left in 1933. In that year Knauer completed his Habilitation. He stayed at Hamburg University where he was appointed to the rank of associate professor in 1939. During the Second World War he contributed to the German nuclear project, the so-called *Uranverein*. After the war he continued working at the institute at Hamburg University till 1963. He died in 1979.

Unlike Otto Stern and Immanuel Estermann, Friedrich Knauer was not of Jewish decent. Thus, he was not forced to leave his position at the University in 1933. However, it is somewhat surprising that Friedrich Knauer signed the *Vow of Allegiance of the Professors of the German Universities and High-Schools to Adolf Hitler and the National Socialistic State*[2] that was presented to the public in Leipzig on November 11, 1933. Also Wilhelm Lenz was among the signatories. Lenz was director of the theoretical physics institute in Hamburg to which Wolfgang Pauli was associated. According to Isidor Rabi's recollections [8], Lenz must have had close ties to Stern's group (see also Ref. [9]). Why did Knauer and Lenz sign the Nazi allegiance? Was it out of conviction, fear or opportunism? And what does it mean with regard to Knauer's relation to Otto Stern and other group members like Estermann, who were forced to leave their positions just a few months earlier? After about nine years of fruitful collaboration on pioneering molecular beam experiments, wouldn't one expect some solidarity, or empathy at least, towards the former colleagues? While seeking answers to these questions is beyond the scope of this contribution, it appears doubtful that the few publicly available documents could provide hints to what the answers might be.

3 The Modern Implementation of the Knauer-Stern Experiment

From the two novel experimental methods introduced in UzM no. 11 only scattering from a crystal surface lead to the observation of matter-wave diffraction, while the scattering from a ruled grating did not. The former methods was used by Otto Stern an his associates in follow-up experiments and allowed them to observe, for instance, the appearance of anomalous dips in diffraction patterns [10]. This phenomenon was

[2] *Bekenntnis der Professoren an den Universitäten und Hochschulen zu Adolf Hitler und dem nationalsozialistischen Staat* überreicht vom Nationalsozialistischen Lehrerbund Deutschland, Gau Sachsen, 1933, Dresden-A. 1, Zinzendorfstr. 2.

later explained in terms of selective adsorption by Lennard-Jones and Devonshire [11] (see Peter Toennies's account on *Otto Stern and Wave-Particle Duality* in this volume), and it was developed into an important method of measuring atom-surface interaction potentials. Following the pioneering experiments in Stern's lab, helium atom scattering from crystal surfaces became a tool in surface science that has found widespread application in many labs around the word [12].

In contrast to the success story of scattering molecular beams off of crystal surfaces, the grating diffraction method was not further pursuit. Otto Stern might have tried the experiment again, had he been able to continue his work in Hamburg. But other groups working with molecular beams might not have considered the grating diffraction experiment worthwhile a try, because the de Broglie wave of atoms and molecules was now well established. As a result, Knauer's and Stern's grating diffraction experiment was pretty much forgotten with time.

The situation started to change in the 1990s when the new field of *atom optics and atom interferometry* [13, 14] emerged. The group of David Pritchard at MIT (Cambridge, MA, USA) first demonstrated diffraction of a beam of sodium atoms from a transmission grating [15]. The grating was a free-standing nanoscale structure with a period of only 200 nm. Fabrication of structures that small had become possible by enormous advances in micro-fanbrication and lithography techniques. Unlike in Knauer's and Stern's experiment, with a free-standing grating the molecular beam could pass through the sub-micron slits with no scattering and (almost) no interaction with the grating material. Thus, reflection from a solid surface was no longer prerequisite to observe the grating diffraction pattern. Subsequently, nanoscale transmission gratings were used in a variety of diffraction experiments with molecular beams of atoms, molecules and clusters including; Na_2 [16], metastable He^* [17], ground-state He, He_2, and He_3 [18, 19], rare-gas atoms [20], CH_3F and CHF_3 molecules [21]. In addition, Markus Arndt and his coworkers at Vienna University were able to observe diffraction patterns of massive and complex particles starting with C_{60} fullerenes [22] (see Markus Arndt's contribution in this volume). A comprehensive review of transmission-grating diffraction experiments as well as the use of transmission gratings in atom and molecular interferometers can be found in the literature [14].

While diffraction of molecular beams from nanoscale transmission gratings was done by several groups, the original Knauer and Stern experiment was not tried until 2007. In the following we describe the setup of the modern-day implementation of the experiment, the results observed and their interpretation.

3.1 Experimental Setup

The molecular-beam apparatus we used in 2007 is shown schematically in Fig. 3 [23]. The legacy of Otto Stern's molecular-beam experiments is still apparent although, of course, various technical implementations of the beam source, detector, vacuum

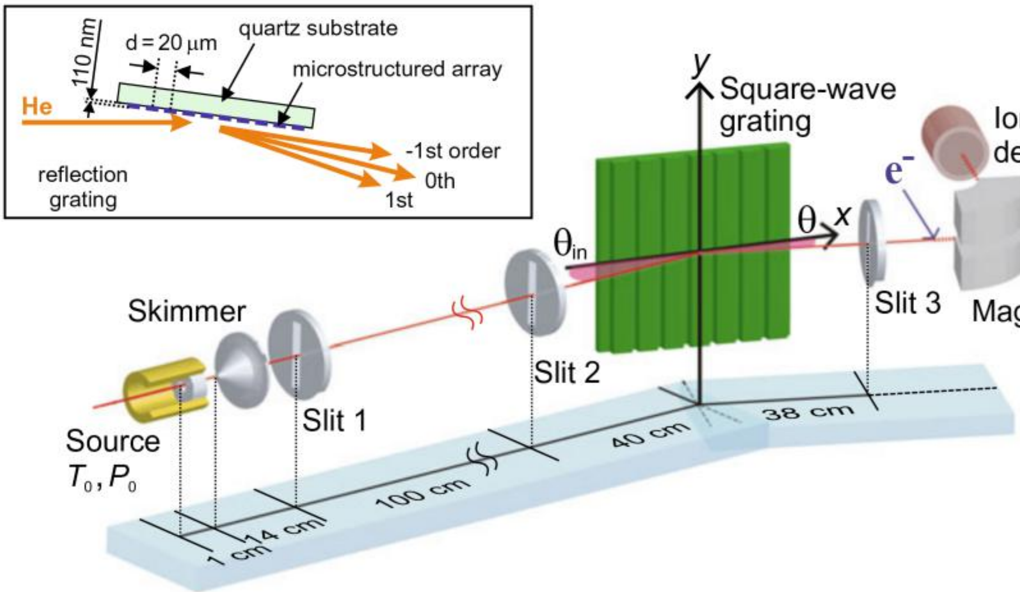


Fig. 3 Schematic of the experimental arrangement used by Zhao et al. in 2007 to observe diffraction of a molecular beam scattering coherently from a reflection grating under grazing incidence conditions [24]. Conceptually, the modern apparatus is essentially analogous to the setup used by Knauer and Stern in 1928, while the technical implementations are different due to, mainly, advances in vacuum and micro-fabrication technologies and in electronics. The inset in the upper left of the figure shows a sketch of the diffraction beams generated at the grating. We use the convention of negative diffraction orders being closer to the grating surface than the specular beam. The incidence angle θ_{in} and detection angle θ are defined with respect to the grating surface plane

system, and the grating are different, not to mention the computerised data acquisition method that was not available to Knauer and Stern.

The beam is formed by free-jet expansion of pure ^{4}He gas from a source cell (stagnation temperature T_0 and pressure P_0) through a 5-μm-diameter orifice into high vacuum. As indicated in Fig. 3, the beam is collimated by two narrow slits, each 20 μm wide, located 15 cm and 115 cm downstream from the source. A third 25-μm-wide detector-entrance slit, located 38 cm downstream from the grating, limits the angular width of the atomic beam to a full width at half maximum of $\approx$ 120 μrad. The detector, which is an electron-impact ionization mass spectrometer, can be rotated precisely around the angle θ indicated in Fig. 3. The reflection grating is positioned at the intersection of the horizontal atom beam axis and the vertical detector pivot axis such that the incident beam approaches under grazing incidence (incident grazing angle $\theta_{in} \leq 20$ mrad), with the grating lines oriented parallel to the pivot axis. Diffraction patterns are measured for fixed incidence angle by rotating the detector around θ and measuring the signal at each angular position. In addition, the grating can be removed from the beam path all together making it possible to measure the direct beam profile, i.e. the undisturbed incident beam, as a function of θ.

Comparison with Stern's apparatus reveals two essential differences beyond mere technological advancements. The first one is the modern molecular beam source. As a consequence of the high stagnation pressure in the source cell combined with the very small 5-μm-diameter aperture, the collision rate of the He atoms in the expanding gas is very large. As a result, the expansion is adiabatic and isentropic leading to a rapid cool down of the gas [25]. A low temperature in the gas is equivalent to a narrow velocity spread in the beam's velocity distribution. The narrowness is often quantified by the *speed ratio* which represents the ratio of mean beam velocity to velocity width. For helium, temperatures below 1 mK and speed ratios of several hundreds have been observed [26, 27]. The expansion efficiently transfers the kinetic energy of the helium gas in the source cell into uniform, directional motion of the molecular beam. As a consequence of de Broglie's formula, Eq. (1), a narrow velocity distribution implies a narrow wavelengths distribution. In other words, the helium beam generated by the modern source is, effectively, monochromatic. In contrast, the effusive beams in the 1920s were characterised by broad velocity and wavelength distributions.

A second qualitative improvement common in most if not all modern-day molecular-beam apparatus is the ionization detector. The neutral He atoms entering the detector are first ionized in collision with electrons of $\simeq 100$ eV kinetic energy. The ions are accelerated by high voltage, mass selected in a magnetic field and finally efficiently detected using a multiplier. The bottle neck of this detection scheme is the inefficient ionization step. It is assumed that only 10^{-6} to 10^{-5} of the neutral He atoms are ionized. However, this poor detection efficiency allows for a far better sensitivity than the Pitot-tube detection scheme that was available to Knauer and Stern in 1928. Interestingly, in an interview given to John L. Heilbron in December 1962 Immanuel Estermann describes that he was trying to build an electron-impact ionization detector in Stern's lab in the early 1920s [28]:

> One of the big problems in molecular beam technology was the (detector) end; we couldn't detect very well. (…) Then, I think, the great step forward was the Langmuir-Taylor detector which was worked out when Taylor was a visiting scientist in Hamburg. But that works only for a limited number of elements or substances. Then we tried all kinds of things, and one of the things that I tried is what is now known as the cross-fire method; it means to bombard the neutral atoms with electrons, thus ionizing them, and then collect the ions. Ions are far easier to detect than the neutral particles. But I did not succeed; I did not get it to work. It's a method which is now used in a number of places quite successfully, but it required much better vacuum technology and much better electronic technology than was available in those days. This must have been about 1923 or '24 when I tried this.

The reflection grating used in 2007 consists of a 56-mm-long micro-structured array of 110-nm-thick, 10-μm-wide, and 5-mm-long parallel chromium strips on a flat quartz substrate. It was made from a commercial chromium mask blank by e-beam lithography. As shown in the inset of Fig. 3 the center-to-center distance of the strips, and thereby the period d, is 20 μm. Given this geometry the quartz surface between the strips is completely shadowed by the strips for all the incidence angles used. We expect a chromium oxide surface to have formed while the grating was exposed to air before mounting it in the apparatus where the ambient vacuum is about 8×10^{-7} mbar. No in-situ surface preparation was done.

3.2 Results

Figure 4 shows a series of diffraction patterns measured with the source kept at $T_0 = 20$ K corresponding to a de Broglie wavelength of $\lambda_{dB} = 2.2$ Å. The incident grazing angle θ_{in} was varied from 3 up to 15 mrad. In each diffraction pattern the specular reflection (0th diffraction-order peak) appears as the strongest peak, for which the detection angle is equal to the incident grazing angle. The intensity of the specular peak decreases continuously from about 600 counts/s at $\theta_{in} = 3.1$ mrad to only 13 counts/s at $\theta_{in} = 15.2$ mrad. At $\theta_{in} = 3.1$ mrad at least seven positive-order diffraction peaks can be seen at angles larger than the specular angle (diffraction 'away from' the surface).

It is straightforward to calculate the nth-order diffraction angle θ_n for given incidence angle θ_{in}, grating period d, and de Broglie wavelength λ_{dB} from the grating equation $\cos(\theta_{in}) - \cos(\theta_n) = n\frac{\lambda_{dB}}{d}$ well known from classical optics [29]. The calculated diffraction angles agree with the observed ones within the experimental error confirming the interpretation of the peaks as grating-diffraction peaks [24]. Note that with increasing incidence angle the negative-order diffraction peaks appear succes-

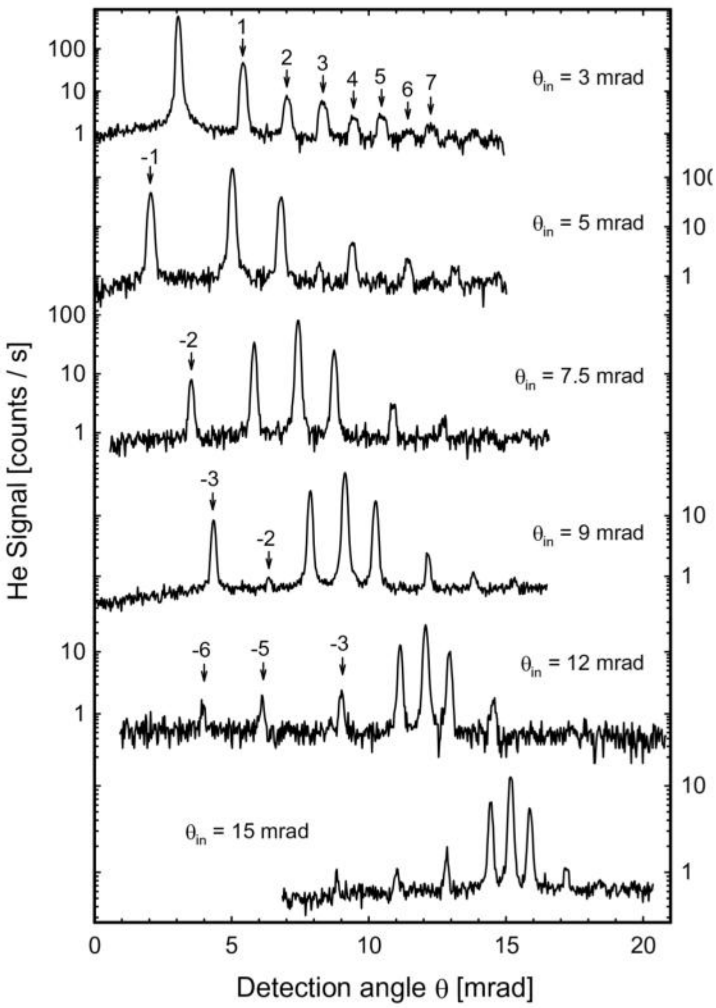


Fig. 4 Diffraction patterns observed for He atom beams of $\lambda_{dB} = 2.2$ Å de Broglie wavelength scattered from a plane grating with 20 μm period at various incidence angles from 3 to 15 mrad (from Ref. [24]). Numbers indicate the diffraction-order assigned to the peaks. In each spectrum the specular peak is most intense. Its peak height decays rapidly with increasing incidence angle

sively, emerging from the grating surface. Emergence of a new diffraction beam comes along with an abrupt redistribution of the flux among the diffraction peaks. These emerging-beam resonances have been studied for He atom beams diffracted by a blazed ruled grating [30].

The relative diffraction peak intensities change significantly with incident grazing angle. For instance, for $\theta_{in} = 3.1$ mrad even and odd order peaks have similar heights falling off almost monotonously with increasing diffraction order. With increasing incident grazing angle, however, the positive even-order diffraction peaks tend to disappear. Moreover, a distinct peak-height variation can be seen for the -2nd-order peak which decreases sharply when θ_{in} is increased from 7.4 to 9.1 mrad.

A diffraction pattern as the ones in Fig. 4 must have been exactly what Otto Stern was longing to see. The data shown here demonstrates that Stern's concept was perfectly viable. What prevented Knauer and Stern from observing diffraction with a machined grating was the limited experimental technology of their time that did not provide the required high beam flux, efficient detection, and high vacuum conditions.

3.3 Quantum Reflection

The peak heights decaying rapidly with increasing incidence angle confirm Otto Stern's conjecture that the highest reflectivity is to be found for the most grazing incidence conditions. A quantitative analysis of the reflectivity dependence on incidence angle is shown in Fig. 5. The reflectivity was determined by summing up the areas of all the peaks in a diffraction pattern. The sum was divided by the area of the direct beam to give the reflectivity. The direct beam (not shown in the plots) is measured when the grating is completely removed from the beam path. The reflectivity at various incidence angles and source temperatures is plotted in Fig. 5 in a semi-logarithmic plot as a function of the incident atoms' wave-vector component perpendicular to the surface, k_{perp}. It is apparent that all the data points fall on a single curve. At small perpendicular wave-vector up to about $0.11\,\text{nm}^{-1}$ the curve decays rapidly, while at values larger than about $0.13\,\text{nm}^{-1}$ it decays at reduced rate.

The same characteristic reflectivity behavior is also found when the diffraction grating is replaced by a plane surface [31]. This behavior cannot be understood by considering a wave scattering off of a rough surface, if one does not include the subtle effects of the atom–surface interaction. The expected dependence in the absence of a surface potential is also plotted in Fig. 5. While the reflectivity in the non-interaction model also tends to unity in the limit of vanishing perpendicular wave vector, this model obviously fails to describe the reflectivity dependence on k_{perp}.

A decent agreement with the observed data is found when quantum reflection from the atom–surface interaction potential is considered. Quantum reflection, just as diffraction, is a wave effect not compatible with the particle picture. The basic idea behind quantum reflection is illustrated in Fig. 6a, b, where the atom–surface interaction potential $V(z)$ is approximated by a square well potential, i.e., $V(z) = \infty$

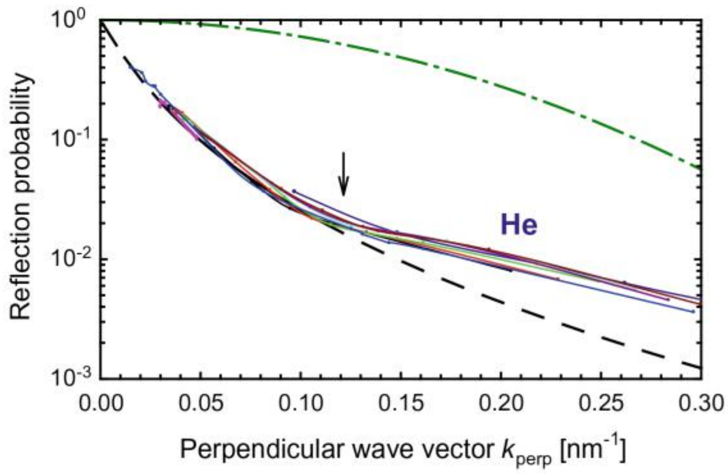


Fig. 5 Reflection probability of He atoms of various de Broglie wavelengths scattering from a plane grating with 20 μm period at a variety of grazing incidence angles plotted as a function of the normal component of the incident atom's wave vector [24]. Each color corresponds to a different wavelength. The dashed line presents a 1-dimensional quantum reflection calculation fitted to the data points at small perpendicular wave vector (left of the arrow). The dash-dotted line represents the reflection probability calculated for a wave scattering from a rough surface (4 nm root-mean-square roughness) in the absence of an atom–surface interaction potential

for $z < a$, $V(z) = 0$ for $z > b$, and $V(z) = V_0$, where V_0 is negative, for $a \leq z \leq b$. Here, the variable z denotes the atom to surface distance, and a and b are positive constants.

Within the classical particle description, Fig. 6a, an incident He atom approaching the well region from positive z with initial kinetic energy E_{kin} will gain energy upon entering the well at $z = b$; its kinetic energy is increased by exactly the well depth V_0. With correspondingly larger velocity the particle slams onto the steep repulsive wall where it is scattered back at the classical turning point. Upon leaving the well its kinetic energy is reduced to its initial value.

The description looks different in the quantum-wave picture, Fig. 6b, if the initial kinetic energy E_{kin} is sufficiently small such that quantum effects become observable. We then have to deal with a wave approaching a step in the potential at $z = b$. As quantum mechanics teaches us, in this situation there is a non-vanishing probability for reflection at the step (even for a "step down" as in our system). This quantum-wave reflection probability increases with increasing de Broglie wavelength of the incident atom. For a discontinuous step, as the one shown in Fig. 6b, it even approaches unity in the limit of vanishing kinetic energy.

The square-well model is a simplistic approximation to an atom–surface potential. In a more realistic model the steps will necessarily be smoothed out, as indicated in the depiction shown in Fig. 6c. Even then, there will be an appreciable reflection probability at the attractive branch of the potential as long as the incident energy of the atom is sufficiently small. This reflection mechanism of matter waves, referred to as quantum reflection, occurs in absence of a classical turning point and, paradoxically,

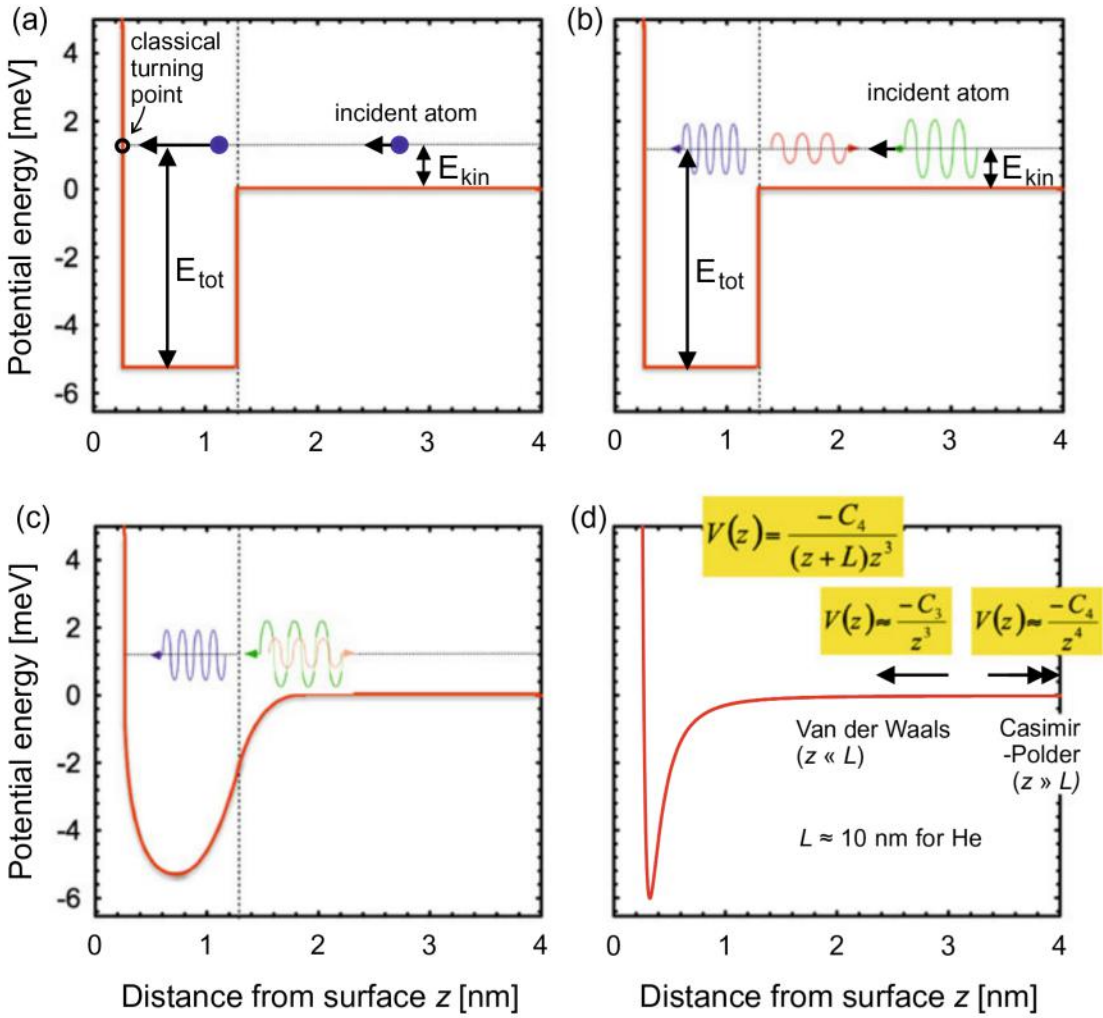


Fig. 6 Illustration of quantum reflection of an atom from a solid surface. In **a** and **b** the atom–surface interaction potential is approximated by a square-well model combined with the classical particle picture (**a**) and the quantum wave picture (**b**). In **c** the square well is smoothened, while **d** shows the potential between a He atom and a silver surface as an actual example. The long-range attractive branch of the potential exhibits a transition from the van der Waals regime at intermedium z to the Casimir–Polder regime at very large z

in the absence of a repulsive force acting on the incoming atom. The latter aspect in particular is counter-intuitive and incompatible with the classical description.

A realistic atom–surface potential model is displayed in Fig. 6d. The example shown describes the interaction between a He atom and a silver surface with a well depth of about 6 meV. The attractive potential branch is modelled by the function $V(z) = \frac{-C_4}{(z+L)z^3}$ describing a Van der Waals–Casimir interaction. The atom specific length L ($L \approx 10$ nm for He) marks the transition from the Van der Waals regime ($V(z) \propto z^{-3}$) at $z \ll L$ to the Casimir–Polder regime ($V(z) \propto z^{-4}$) at $z \gg L$. Although this potential looks smooth, it can be shown that its quantum reflection probability will approach unity in the zero-energy limit [32].

Quantum reflection of atoms from a solid surface was described by theory [32–38]. It was first observed in experiments with ultracold metastable atoms [39] and, later, also with a Bose-Einstein condensate [40, 41]. In these experiments extremely small atomic velocities needed to observe quantum reflection are achieved by cooling a dilute atomic gas in a trap to ultracold temperatures. An alternative approach to achieve those velocities is to scatter an atomic or molecular beam from a solid at grazing incidence [24, 31, 42], Due to the grazing incidence geometry the relevant velocity z-component, perpendicular to the surface, can approach extremely small values allowing observation of quantum reflection. The comparatively large parallel velocity component does not affect the quantum reflection process as long as the surface is (at least locally) homogenous. Quantum reflection of helium beams from plane surfaces [31, 42] as well as laminar [24] and blazed ruled [30] gratings has been reported.

In addition, reflection and diffraction from a grating was also observed for weakly bound ground-state helium dimers (He_2 binding energy ≈ 0.1 μeV) and trimers (He_3 binding energy ≈ 10 μeV) [43, 44]. Following the above description of classical scattering, the forces in the molecule–surface potential well region will inevitably lead to bond breakup, because the well depth (order of magnitude 10 meV) is $\approx 10^5$ times and $\approx 10^3$ times larger than the binding energy of helium dimers and trimers, respectively. Therefore, the observation of reflection of dimers and trimers provides direct evidence for quantum reflection. Furthermore, the fact that diffraction patterns are found indicates that quantum reflection leads to coherent reflection of matter waves.

4 Conclusion

The experiment described by Friedrich Knauer and Otto Stern in the UzM no. 11 article was designed to observe matter-wave diffraction of He and H_2 beams scattering off of a ruled diffraction grating at grazing incidence conditions. They were able to observe mirror-like, specular reflection with the reflectivity increasing with decreasing incidence angle and with increasing de Broglie wavelength. But, they fell short of detecting diffraction peaks. The modern reincarnation of the experiment was performed in 2007 in the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin, Germany. Conceptually, the modern apparatus is in line with the setup used in Otto Stern's lab. Yet, its intense molecular-beam source and sensitive electron-impact ionization detector out-perform their 1920s counterparts. In combination with better vacuum systems and modern electronics this made it possible to observe fully resolved diffraction patterns of He atom beams including peaks up to the seventh diffraction order. It can be assumed that the diffraction pattern observed in 2007 was exactly what Knauer and Stern were hoping to observe.

The results gained with the modern equipment make it clear that Knauer's and Stern's experiment was well conceived; it was bound to work, as soon as sufficient signal was available. This holds despite the fact that Otto Stern and his coworkers did not know that the atom–surface interactions can lead to quantum reflection and, thus, play a crucial role in the coherent scattering of atoms and molecules from surfaces.

While they did consider atom–surface interactions in the context of diffraction from a cleaved crystal surface, they ignored it for the gratings. It might well be that Friedrich Knauer and Otto Stern were the first to observe, unknowingly, quantum reflection of atoms from a solid surface more than 80 years before the first conclusive demonstration of this effect by Shimizu [39]. Ironically, quantum reflection itself is a wave phenomenon that cannot be explained with particles. As such, observation of quantum reflection of atoms provides evidence for de Broglie waves of an atom, exactly what Otto Stern was aiming to observe.

Acknowledgements I am indebted to my long-term collaborator, Prof. Bum Suk Zhao (UNIST, Ulsan, South Korea). His hard and skilful work was crucial to succeed with our joint diffraction experiments described in this contribution. I also want to thank Prof. Peter Tonnies (Max-Planck-Institut für Dynamik und Selbstorganisation, Göttingen, Germany). As my thesis adviser he taught me the art of running molecular-beam experiments; the legacy from Otto Stern a century ago. Furthermore, I thank Prof. Gerard Meijer (Fritz-Haber-Institut (FHI) der Max-Planck-Gesellschaft, Berlin, Germany) for making it possible for me to pursue molecular-beam diffraction experiments at the FHI. Last not least, I thank Prof. Bretislav Friedrich (FHI, Berlin, Germany) for numerous revealing discussions on Otto Stern and his legacy, and I want to thank him as well as Prof. Horst Schmidt-Böcking (Goethe Universität, Frankfurt, Germany) for their effort of organising this one-of-a-kind Otto-Stern tribute.

References

1. L. de Broglie, Recherches sur la théorie des quanta. Annales de Physique **10**, 22–128 (1925)
2. F. Knauer, O. Stern, The Reflection of Molecular Beams. Zeitschrift für Physik **53**, 779–791 (1929)
3. M. Eckert, Max von Laue and the discovery of X-ray diffraction in 1912. Ann. Phys. **524**, A83–A85 (2012)
4. I. Estermann, O. Stern, Diffraction of molecular beams. Zeitschrift für Physik **61**, 95–125 (1930)
5. I. Estermann, R. Frisch, O. Stern, Molecular ray problems. Experiments with monochromatic de Broglie waves of molecular beams. Physikalische Zeitschrift **32**, 670–674 (1931)
6. O.R. Frisch, O. Stern, *Handbuch der Physik*, ed. by H. Geiger, K. Scheel, Vol. XXII, II. Teil (Negative und positive Strahlen), 2 edn. (Springer, Berlin, Germany, 1933) , pp. 313–354
7. F. Knauer, O. Stern, Intensity measurements on molecular beams of gases. Zeitschrift für Physik **53**, 766–778 (1929)
8. T.S. Kuhn, Interview of I.I. Rabi (1963). Available online at www.aip.org/history-programs/niels-bohr-library/oral-histories/4836
9. J.P. Toennies, H. Schmidt-Böcking, B. Friedrich, J.C.A. Lower, Otto Stern (1888–1969): the founding father of experimental atomic physics. Ann. Phys. (Berlin) **523**, 1045–1070 (2011)
10. R. Frisch, O. Stern, Abnormality in the specular reflection and diffraction of molecular beams of crystal cleavage planes. I. Zeitschrift für Physik **84**, 430–442 (1933)
11. J.E. Lennard-Jones, A.F. Devonshire, Diffraction and selective adsorption of atoms at crystal surfaces. Nature **137**, 1069–1070 (1936)
12. G. Benedek, J.P. Toennies, *Atomic Scale Dynamics at Surfaces: Theory and Experimental Studies with Helium Atom Scattering* (Springer, Berlin, Germany, 2018)
13. P.R. Berman (ed.), *Atom Interferometry* (Academic Press, New York, 1997)
14. A.D. Cronin, J. Schmiedmayer, D.E. Pritchard, Optics and interferometry with atoms and molecules. Rev. Mod. Phys. **81**, 1051–1129 (2009)

15. D.W. Keith, M.L. Schattenburg, H.I. Smith, D.E. Pritchard, Diffraction of atoms by a transmission grating. Phys. Rev. Lett. **61**, 1580 (1988)
16. M.S. Chapman, et al., Optics and interferometry with Na_2 molecules. Phys. Rev. Lett. **74**, 4783 (1995)
17. O. Carnal, A. Faulstich, J. Mlynek, Diffraction of metastable helium atoms by a transmission grating. Appl. Phys. B **53**, 88 (1991)
18. W. Schöllkopf, J.P. Toennies, Nondestructive mass selection of small van der Waals clusters. Science **266**, 1345 (1994)
19. W. Schöllkopf, J.P. Toennies, The nondestructive detection of the helium dimer and trimer. J. Chem. Phys. **104**, 1155 (1996)
20. R.E. Grisenti, et al., Determination of atom-surface van der Waals potentials from transmission-grating diffraction intensities. Phys. Rev. Lett. **83**, 1755–1758 (1999)
21. W. Schöllkopf, R.E. Grisenti, J.P. Toennies, Time-of-flight resolved transmission-grating diffraction of molecular beams. Eur. Phys. J. D **28**, 125 (2004)
22. M. Arndt, O. Nairz, J. Vos-Andreae, C. Keller, G. van der Zouw, A. Zeilinger, Wave-particle duality of C_{60} molecules. Nature **401**, 680 (1999)
23. This apparatus was built in the 1990s in Prof. J.P. Toennies's Dept. of Molecular Interactions in the Max-Planck-Institut für Strömungsforschung in Göttingen, Germany, and was relocated to the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin, Germany in 2005 where it has been in use since then
24. B.S. Zhao, S.A. Schulz, S.A. Meek, G. Meijer, W. Schöllkopf, Quantum reflection of helium atom beams from a microstructured grating. Phys. Rev. A **78**, 010902(R) (2008)
25. H. Buchenau, E.L. Knuth, J. Northby, J.P. Toennies, C. Winkler, Mass spectra and time-of-flight distributions of helium cluster beams. J. Chem. Phys. **92**, 6875 (1990)
26. J. Wang, V.A. Shamamian, B.R. Thomas, J.M. Wilkinson, J. Riley, C.F. Giese, W.R. Gentry, Speed ratios greater than 1000 and temperatures less than 1 mk in a pulsed He beam. Phys. Rev. Lett. **60**, 696–699 (1988)
27. L.W. Bruch, W. Schöllkopf, J.P. Toennies, The formation of dimers and trimers in free jet ^{4}He cryogenic expansions. J. Chem. Phys. **117**, 1544–1566 (2002)
28. J.L. Heilbron, Interview of Immanuel Estermann (1962). Available online at www.aip.org/history-programs/niels-bohr-library/oral-histories/4593
29. M. Born, E. Wolf, *Principles of Optics*, 6th edn. (Cambridge University Press, Cambridge, 1997)
30. B.S. Zhao, G. Meijer, W. Schöllkopf, Emerging beam resonances in atom diffraction from a reflection grating. Phys. Rev. Lett. **104**, 240404 (2010)
31. B.S. Zhao, H.C. Schewe, G. Meijer, W. Schöllkopf, Coherent reflection of He atom beams from rough surfaces at grazing incidence. Phys. Rev. Lett. **105**, 133203 (2010)
32. H. Friedrich, G. Jacoby, C.G. Meister, Quantum reflection by Casimir-van der Waals potential tails. Phys. Rev. A **65**, 032902 (2002)
33. R.B. Doak, A.V.G. Chizmeshya, Sufficiency conditions for quantum reflection. Europhys. Lett. **51**, 381–387 (2000)
34. A. Mody, M. Haggerty, J.M. Doyle, E.J. Heller, No-sticking effect and quantum reflection in ultracold collisions. Phys. Rev. B **64**, 085418 (2001)
35. S. Miret-Artés, E. Pollak, Scattering of He atoms from a microstructured grating: quantum reflection probabilities and diffraction patterns. J. Phys. Chem. Lett. **8**, 1009–1013 (2017)
36. J. Petersen, E. Pollak, S. Miret-Artés, Quantum threshold reflection is not a consequence of a region of the long-range attractive potential with rapidly varying de Broglie wavelength. Phys. Rev. A **97**, 042102 (2018)
37. G. Rojas-Lorenzo, J. Rubayo-Soneira, S. Miret-Artés, E. Pollak, Quantum reflection of rare-gas atoms and clusters from a grating. Phys. Rev. A **98**, 063604 (2018)
38. G. Rojas-Lorenzo, J. Rubayo-Soneira, S. Miret-Artés, E. Pollak, Quantum threshold reflection of He-atom beams from rough surfaces. Phys. Rev. A **101**, 022506 (2020)
39. F. Shimizu, Specular reflection of very slow metastable neon atoms from a solid surface. Phys. Rev. Lett. **86**, 987–990 (2001)

40. T.A. Pasquini, et al., Quantum reflection from a solid surface at normal incidence. Phys. Rev. Lett. **93**, 223201 (2004)
41. T.A. Pasquini, et al., Low velocity quantum reflection of Bose-Einstein condensates. Phys. Rev. Lett. **97**, 093201 (2006)
42. V. Druzhinina, M. DeKieviet, Experimental observation of quantum reflection far from threshold. Phys. Rev. Lett. **91**, 193202 (2003)
43. B.S. Zhao, G. Meijer, W. Schöllkopf, Quantum reflection of He_2 several nanometers above a grating surface. Science **331**, 892–894 (2011)
44. B.S. Zhao, W. Zhang, W. Schöllkopf, Non-destructive quantum reflection of helium dimers and trimers from a plane ruled grating. Mol. Phys. **111**, 1772–1780 (2013)