Nobel Physics Prize to Bloembergen, Schawlow and Siegbahn

The 1981 Nobel prize in physics has been awarded to Nicolaas Bloembergen of Harvard University, Arthur L. Schawlow of Stanford University and Kai M. Siegbahn of Uppsala University. Bloembergen and Schawlow will receive half the prize "for their contribution to the development of laser spectroscopy." The other half will go to Siegbahn "for his contribution to the development of high-resolution electron spectroscopy." The prize, to be awarded in Stockholm on 10 December, this year amounts to one million Swedish kroner (worth about $180 000).

Masers. In the early 1950s, workers in the US and the Soviet Union were trying to make use of stimulated emission in molecular systems to amplify weak microwave signals and to design oscillators based on such systems. This work led to the maser, first demonstrated by Charles Townes and his collaborators in the US; at the same time the maser had been suggested by Nikolai Basov and Alexander Prokhorov in the Soviet Union.

Schawlow told us that he and Townes (his future brother-in-law) shared a hotel room at the APS Washington meeting in Spring, 1951. To avoid disturbing Schawlow's sleep one morning, Townes sat outside on a park bench and worked out the idea for the ammonia maser. Three years later, Townes, James Gordon and Herbert J. Zeiger reported the operation of such a maser.

In 1948, Bloembergen recalled as we sat in his Harvard office, he, Edward M. Purcell and Robert V. Pound published a paper on relaxation effects in nuclear magnetic resonance. In this work, they "burned a hole" in the nmr spectrum of protons in water in an inhomogeneous magnetic field and obtained a narrow dip. Later, in 1963, a closely related spectral hole-burning effect in lasers (based on an inhomogeneous velocity distribution rather than an inhomogeneous spatial distribution) was discovered independently by William Bennett Jr, Willis Lamb and R. A. McFarlane and independently by Abraham Szoke and Ali Javan. This so-called Lamb dip is the basis of laser saturation spectroscopy because it allows one to get rid of Doppler broadening and to determine the center of a spectral line with great accuracy. These line-narrowing phenomena in inhomogeneous systems also allow one to take advantage of magnetic resonance in organic materials and in liquids.

Work on magnetic resonance led Purcell and Pound to introduce in 1950–51 the ideas of inverted popula-

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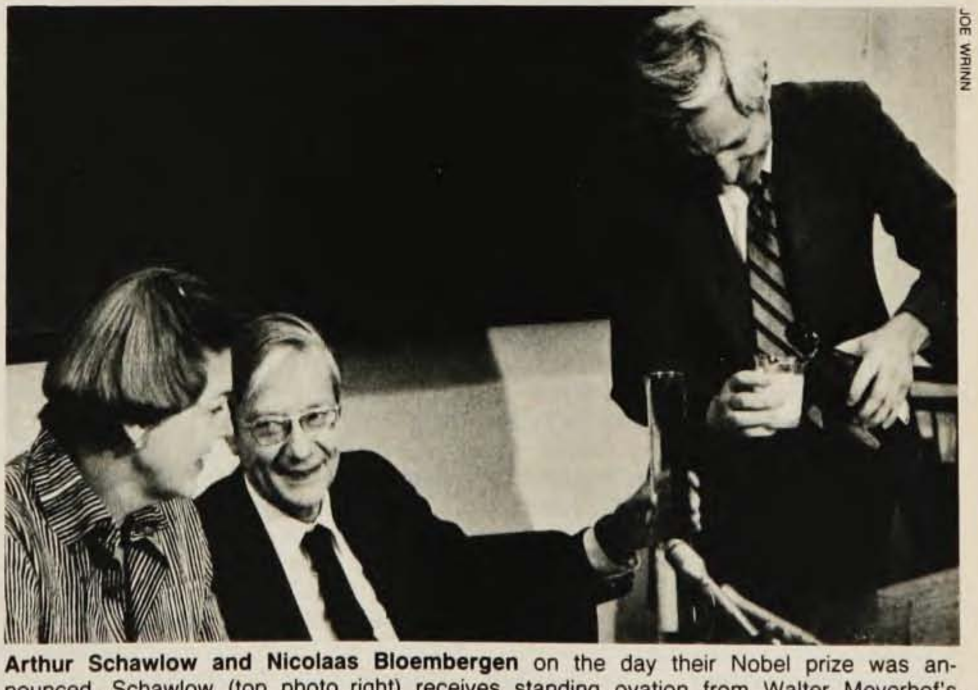

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Arthur Schawlow and Nicolaas Bloembergen on the day their Nobel prize was announced. Schawlow (top photo, right) receives standing ovation from Walter Meyerhof's physics class at Stanford. Bloembergen (bottom photo, center), at Harvard press conference, shares champagne with his wife Deli and Paul Martin.

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tions and negative temperatures. In 1953 Albert Overhauser found the effect that now bears his name, an effect in which you saturate the electron spin transitions in a metal and get a very large change in population distributions between the nuclear spin levels. Inspired by these discoveries, Bloembergen in 1956 developed the concept of a three-level solid-state maser. To make a steady-state inverted population, one takes advantage of the combined action of a "hot" pump and relaxation to a "cold" reservoir. Bloembergen argued that masers can be considered as a type of heat engine operated between two temperatures. The hot and cold temperatures occur in the same volume element in space, unlike that of the usual thermodynamic engines, in which there is a hot part in which fuel is burned and another part where the system is cooled.

Schawlow told us the first really useful maser was Bloembergen's proposal. Although the ammonia maser was useful for atomic clocks, it was not yet a broadband, tunable low-noise amplifier. Following Bloembergen's proposal of the three-level maser, the first such solid-state maser was demonstrated by Derrick Scovil, George Feher and Harold Seidel at Bell Labs using lanthanum ethyl sulfate doped with gadolinium and cerium. Bloembergen built a solid-state maser using $CoK_3(CN)_6$ doped with chromium. A ruby maser was built by three groups, one of them headed by Townes. Bloembergen reminisced about the occasion in 1959 when he and Townes received the Morris Leibmann award for contributions to the maser art. Townes had presented his wife, Frances, with a medallion made from the ruby he used for his maser. When Bloembergen's wife, Deli, admired the medallion and asked for a similar memento of *his* maser, he said, "Well, dear, my maser works with cyanide."

The solid-state maser had low noise and could be tuned with a magnetic field because of its unpaired spins. The multi-level pumping scheme led to the development of low-noise microwave receivers. One such maser was used by Arno Penzias and Robert W. Wilson in 1965 to discover the 3-K blackbody radiation from the Big Bang. Subsequently all lasers have used similar schemes in a combination of multilevel pumping and relaxation.

Laser spectroscopy. The Swedish Academy of Sciences notes that the idea of extending the maser principle to the infrared or optical region "arose in different quarters in the late 1950s. The wholly decisive contribution in the realization of this idea was made in 1958 by Schawlow and Townes, who then published a work analyzing the preconditions necessary for such a design, theoretical as well as practical. Prokhorov around the same time proposed a similar design for the generation of longer waves. Other suggestions based on the same idea were also presented at that time. However, it was primarily the work by Schawlow and Townes which initiated the whole dynamic field which we now associate with the concept of 'laser.'" The Academy also noted that although the 1964 Nobel prize in physics was awarded to Townes, Prokhorov and Basov for "fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser–laser principle," subsequent developments, particularly in lasers, "have made this field increasingly deserving of additional rewards."

Starting in mid-1957, Schawlow recalls, he and Townes analyzed the problems of extending the maser to shorter wavelengths. By December 1958 they had shown the possibility of making an optical maser with a structure that had mirrors on either side of the cavity. The race to build the first one was won by Theodore Maiman in Spring 1960; he used light ruby, taking advantage of isolated chromium ions. During the race, Schawlow told us, he outsmarted himself, believing that because no one had yet made a laser, it was difficult to make one work. So he tried using pairs of chromium ions, a more complex approach than Maiman used. By the end of 1960, five different lasers were operating, including Schawlow's.

The Swedish Academy notes that Schawlow and his coworkers at Stanford have emphasized the kind of nonlinear spectroscopy based on saturation phenomena, which occur in the absorption of laser light because of its high intensity. Schawlow told us that even in his 1958 paper with Townes they had mentioned that lasers could be used for spectroscopy provided one could get some degree of tunability, but narrow lines were needed for high gain in the laser. During the 1960s, he said, some spectroscopy was done to investigate the details of the same lines as those producing the laser action, such as the neon line in the He–Ne laser.

A particularly sensitive and simple method of saturated absorption spectroscopy now known as the Hänsch–Bordé method was used in 1970 by Christian Bordé in Paris and independently in Stanford by Theodor W. Hänsch, Marc D. Levenson, Schawlow and Peter Smith, following earlier experiments at the University of Heidelberg by Hänsch and Peter Toschek. The absorbing gas sample is kept in a cell outside the laser resonator. The beam is split into a strong saturating beam and a weaker probe beam, which are sent by mirrors in nearly opposite directions through the absorber. When the saturating beam is on, it bleaches a path through the cell, allowing the probe signal to be received more strongly at the detector. The probe signal will be modulated when the laser is tuned near the center of the Doppler-broadened absorption line, so that both beams interact with the same atoms. This approach eliminates Doppler broadening due to motion of the atoms.

Schawlow recalls that initially he had failed to see the advantages of using the high intensity of one laser to produce lasing action in another medium. In 1966, at IBM, Peter Sorokin made a laser from an organic dye; similar work was done by Fritz Schäfer at the University of Marburg. The organic dye laser made broadband tunability possible; the high light intensity needed to pump the dyes is most easily obtained from another laser. In 1971 Hänsch, Issa Shahin and Schawlow used a pulsed dye laser pumped by a nitrogen laser; they introduced a telescope to expand the beam and an etalon for very fine tuning. The result was linewidths as narrow as 300 MHz (5 parts in 10^7).

In 1972 the same three Stanford collaborators used a pulsed laser and the external saturation method to observe for the first time Doppler-free optical spectra of hydrogen. They obtained optical resolution of the Lamb shift, allowing a precision measurement of the absolute wavelength of the hydrogen lines. Thus they were able to determine the Rydberg constant with much higher precision than previously possible (initially a factor of ten better). Every couple of years since, the determination of the Rydberg constant has improved by factors of two or three.

In 1974 Bernard Cagnac in France, Bloembergen and Levenson at Harvard and Hänsch, G. Maisel, Ken C. Harvey and Schawlow all showed the feasibility of Doppler-free two-photon spectroscopy. (The idea had earlier been suggested by Veniamin Chebotayev.) In this form of high-resolution nonlinear laser spectroscopy, gas atoms in a standing-wave field are excited by absorbing two photons from opposite directions. Their first-order Doppler shifts are equal and opposite; so the sum frequency is unchanged.

The use of lasers to detect trace elements was pioneered by William Fairbank Jr, Hänsch and Schawlow. In 1975 they were able to detect resonance fluorescence from sodium atoms when as few as 100 atoms/cm^3 were present (or as little as one atom at a time in the beam).

In 1976 Schawlow and his collaborators started using lasers to simplify complicated spectra. The technique is now known as lower-level labeling or population labeling; it has been extended to include polarization labeling.

Asked to compare and contrast his work with that of Bloembergen over the past two decades, Schawlow said the Stanford workers have been trying to simplify spectra, eliminate Doppler broadening and do it very sensitively with a small number of atoms and molecules. They have concentrated on changing populations of stationary states. On the other hand, he said, Bloembergen and his collaborators have been concentrating on changing the susceptibility of a medium by nonlinear optics. The Harvard workers have emphasized bulk properties (which are of course determined by atoms) whereas the Stanford workers have emphasized individual atomic and molecular levels.

Bloembergen told us that since lasers were first built in 1960 he has been exploiting them to study the properties of matter at high light intensities, particularly after 1961, when Peter Franken and his collaborators demonstrated second harmonic generation of light, in which red light from a ruby had its wavelength halved to the ultraviolet. This discovery opened the field of nonlinear optics to experimenters. Bloembergen noted that lots of nonlinear effects were already known from the work done shortly after World War II with microwave spectroscopy, nuclear magnetic resonance and electron paramagnetic resonance.

Two papers in 1962 by Bloembergen and his collaborators—John A. Armstrong, Jacques Ducuing and Peter S. Pershan—developed a general framework to describe a large number of nonlinear optical phenomena applicable to liquids, semiconductors, metals and so on. The electric polarization can be expanded in a power series in **E**, the electric-field amplitudes.

$$\mathbf{P} = \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{EE} + \chi^{(3)}\mathbf{EEE} + \ldots$$

$\chi^{(1)}$ is the linear susceptibility and $\chi^{(2)}$ is the lowest-order nonlinear susceptibility, a third-rank tensor.

In 1964 Bloembergen and Yuen-Ron Shen worked out analogies to the Kramers–Heisenberg relation for nonlinear behavior, including damping for nonlinear susceptibilities and showing the properties of the imaginary parts of the equation. Then, Bloembergen told us, he and his collaborators did experiments to back up the theory. For example, in 1969 Bloembergen and Hansen Shih predicted the nonlinear analog to conical refraction (whose theory had been developed by William R. Hamilton in 1833); in 1977 Anita Schell and Bloembergen observed nonlinear conical refraction.

The Swedish Academy announcement singled out the contributions of Bloembergen and his collaborators to four-wave mixing, in which three coherent light waves act together to produce a fourth light wave in a new direction. Although first demonstrated experimentally by Robert W. Terhune and his collaborators at Ford Research Labs, Bloembergen and his collaborators have studied four-wave mixing systematically as a function of the three frequencies in many different materials and obtained the dispersive characteristics. By varying the angle between beams, one can also vary the wave vectors and alter the polarization of each beam. "Clearly, nonlinear properties are a much richer field than linear spectroscopy," Bloembergen remarked.

One example of four-wave mixing is phase conjugation. Bloembergen and his collaborators recently used four light beams of almost equal frequency to show the effect of collision-induced coherence, a paradoxical behavior because collisions usually destroy coherence. Another example of four-wave mixing is Coherent Anti-Stokes Raman Scattering or "CARS," a technique developed by Bloembergen and various Harvard collaborators and done in many other labs.

Electron spectroscopy. The Nobel prize in physics to Kai Siegbahn is in a sense the first to be given for surface physics since Clinton Davisson was honored in 1937. Kai Siegbahn's father, Manne Siegbahn, received the Nobel prize in physics in 1925 for the development of high-resolution x-ray spectroscopy. The son is honored this year for the development of high-resolution electron spectroscopy.

As early as 1913, H. Robinson in Ernest Rutherford's lab in Manchester had used photoelectron spectroscopy to obtain information on the electron structure of a given sample. Despite two decades of work, Robinson, because he did not have a high-resolution spectrometer, could not distinguish an elastic from an inelastic peak in a plot of intensity *vs.* electron kinetic energy. Because of the relatively low resolution, photoelectron spectroscopy for materials research was considered less useful than x-ray spectroscopy until the 1950s, the Swedish Academy said.

In the mid-1950s, Kai Siegbahn and his collaborators at Uppsala, Carl Nordling and Evelyn Sokolowski, began analyzing photoelectrons with the aid of a high-resolution double-focusing spectrometer, originally designed for nuclear beta-ray spectroscopy. Because the spectrometer was iron-free, its magnetic field was directly proportional to the coil current. The spectrometer had high accuracy and stability (so spectral lines did not drift during a measurement) and a resolution a factor of ten better than previously available.

Until the work of Siegbahn and his collaborators the binding energies of

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core electrons of atoms were not well known. Previously, these binding energies had been found through x-ray absorption, in which one measures the position of an absorption edge rather than a peak. Finding the edge had limited the accuracy of the x-ray absorption method as well as earlier photelectron spectroscopy until the Uppsala work. The group in Uppsala irradiated a sample with x rays having a characteristic line spectrum. (One popular line is the copper $K\alpha$ line at about 8 keV.) These x rays expel electrons from atomic levels in the target, and these electrons undergo energy losses through inelastic scattering on their way out of the target. At low electron-energy resolution such as used by Robinson, the inelastically scattered electrons could not be distinguished from the elastically scattered electrons. The resulting spectrum had an edge shape similar to an absorption spectrum.

The Uppsala group discovered that at very high resolution the inelastically scattered electrons are well separated from the elastic peak because the energy-loss mechanism is quantized in energy. The resulting electron spectrum therefore shows very well-defined peaks (electron lines) corresponding to the various atomic levels of the target. The widths of these peaks are determined by the natural width of the atomic levels. In this way the kinetic energy of the photoelectrons could be measured very precisely and the atomic binding energies could be deduced with high accuracy.

During the late 1950s Siegbahn, Nordling and Sokolowski made a systematic study of electron binding energies in different elements, a study which is still a major source of information on inner atomic levels.

In 1958 Stig Hagstrom (now at Xerox

Research Center and Stanford) joined the group, which started to work on developing photoelectron spectroscopy for quantitative elemental analysis of light elements.

In a compound such as Na_2SO_4 one will observe a peak from sodium, a peak from sulfur and a peak from oxygen. By measuring relative intensities and knowing the composition, one could calibrate the spectrometer, allowing one to study unknown materials. In 1964, while they were studying Na_2SO_4, partly by mistake and partly for convenience, Hagstrom recalled to us, he, Nordling and Siegbahn looked at $Na_2S_2O_3$. In this compound the two sulfur atoms are in two different chemical positions, one in the $+6$ and the other in the -2 oxidation state. From the sulfur K level in fact they saw two peaks, and they realized that one came from the $+6$ state and the other from -2. Chemical shifts had previously been seen in x-ray absorption and also by Nordling, Siegbahn and Sokolowski in 1957. At that time the group thought the shift was from changes in valence electrons. But through the double peak from the sodium thiosulfate compound it became obvious that the core level was shifted, not the valence.

These chemical shifts in core levels were caused by a difference in the way the atom was bound in the molecule or crystal, that is, the different electron densities in the vicinity of the atoms. Similar shifts had been seen in x-ray spectra but were much more subtle and difficult to interpret. The Swedish Academy notes that "in the development of electron spectroscopy, a practically useful analytical method had been obtained [by the Uppsala group] with which it was possible to study not only which atoms are included in a sample but also in what chemical environment these atoms exist. At this time the concept of 'ESCA' (Electron Spectroscopy for Chemical Analysis) was created. . . " Siegbahn and his collaborators immediately realized the great potentiality of ESCA. Not only would it be useful for quantitative elemental analysis (how much of a given element is present), it would also be sensitive to various oxidation states of an element.

The early Uppsala work was done on various elements and compounds. After finding the chemical-shift effect, they made a systematic study of noble gases and simple gases such as CO and CO_2. Later they went on to study solids. About 1973–74, in a *tour de force*, Siegbahn and his collaborators did ESCA on liquids, employing a continuous wire (attached to a pulley), which dipped into the liquid bath. Above the liquid surface was an x-ray tube. The group observed photoelectrons from the wet wire.

X-ray photoelectron spectroscopy (also called XPS) allows one to study the outermost several atomic layers (between two and ten layers or 5–20 Å). After the Siegbahn group's original work on ESCA it was realized that one can optimize the surface sensitivity by using grazing take-off angles. To study the composition of deeper layers, one can remove surface atoms. By sputtering with argon ions, for example, one can remove surface atoms and obtain the composition as a function of depth. Such probing can also be done by mechanical or chemical means, depending on how deep one wishes to probe. However, all these removal techniques can leave undesirable artifacts, for example, decomposing a chemical compound. One advantage of ESCA is that the incident x rays are not very damaging compared to the electron beams used with Auger-electron spectroscopy of surfaces.

After the discovery of the chemical shift by Siegbahn and his collaborators, a number of other labs became involved. One such group was established in 1964 by Manfred Krause and Thomas Carlson at Oak Ridge. Another was the group at Berkeley started in 1965 by Hagstrom, Charles Fadley, David Shirley and Jack Hollander.

By the late 1960s, several commercial companies started making instruments for ESCA. By now photoelectron spectroscopy is being applied in various forms at hundreds of labs. It has been used for studies of many surface-chemistry processes such as catalysis and corrosion.

Meanwhile synchrotron radiation sources have become increasingly available, allowing one to tune the x-ray energy. Thus one can improve surface sensitivity by choosing the photoelectron energy to correspond to the minimum mean free path for a given material.

Vital statistics. Bloembergen received a BA in 1941 and an MA in physics in 1943, both from the University of Utrecht. In 1946 he went to Harvard, where he did his thesis with Purcell. His PhD was awarded in 1948 from the University of Leiden. From 1949 to 1951 he was a junior fellow in the Society of Fellows at Harvard, where he has been ever since, except for visiting professorships. Since 1957 he has been Gordon McKay Professor of Applied Physics and since 1980 Gerhard Gade University Professor.

Schawlow earned all three degrees at the University of Toronto, BA in 1941, MA in 1942 and PhD in 1949. At that time he became a research associate at Columbia University, staying until 1951, when he joined Bell Labs. He remained there until 1961. He then joined Stanford where he served as department chairman 1966–70. Since 1978 he has been J. G. Jackson–C.J. Wood Professor of Physics at Stanford. He was president of the Optical Society of America in 1975 and is president this year of The American Physical Society.

Siegbahn earned his PhD at Stockholm University in 1944. Since 1954 he has been professor of physics at Uppsala University. —GBL

Chemistry Prize to Fukui and Hoffmann

The Royal Swedish Academy of Sciences has awarded the 1981 Nobel prize in chemistry jointly to Kenichi Fukui of Kyoto Imperial University and Roald Hoffmann of Cornell. The two theoretical chemists are cited by the Academy "for their theories, developed independently, concerning the course of chemical reactions." Both men have used similar perturbation-theoretic approaches to the quantum theory of molecular bonding to develop useful techniques for the understanding and prediction of reaction rates and geometrical configurations in molecular reactions. Their ideas stress the conservation of spatial symmetries of electron wavefunctions as bonds are altered in the process of molecular rearrangement.

Although these techniques have proven to possess enormous predictive power, especially for the carbon–carbon bonds of organic molecules, Fukui's early work, before 1965, was expressed in a mathematical formalism that attracted little attention among laboratory organic chemists accustomed to thinking in terms of stick models rather than equations heavy with subscripts and superscripts.

In 1965, Hoffmann, working with Robert B. Woodward (Harvard), whom he describes as "the premier organic chemist of his time," published a set of rules for the qualitative prediction of reaction rates and bond geometries, similar to Fukui's independent line of thought, but formulated in a simple, almost pictorial way that made them particularly useful to laboratory chemists without requiring detailed calculations. Since their first appearance, these "Woodward–Hoffmann rules" have been widely applied to a great variety of molecular reactions, especially organic and organometallic processes. "They have revolutionized the way organic chemists think about reactions," we were told by Kendall Houk