

# The Creative Kohn

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So what is common between the two scientists who shared the Chemistry Nobel Prize, 1998?

They both have a) studied in UK, b) worked at Carnegie Mellon University, Pittsburgh for several years, c) remained active in one specific research field for over three decades, d) had a good number of Indian graduate students, e) received post-graduate degrees in subjects other than chemistry, f) made several significant contributions to science besides that cited in Nobel Prize, g) had the most stimulating teachers and thesis supervisors, some of them also Nobel Prize winners.

These two scientists are: Walter Kohn, University of California at Santa Barbara, USA and John A Pople, Northwestern University, Evanston, Illinois, USA. The award citation reads “to Walter Kohn for his development of the density-functional theory and to John Pople for his development of computational methods in quantum chemistry.” Since the early work of Heitler and London in 1927, scientists and mathematicians have greatly contributed towards the understanding of how bonds between atoms and molecules operate. R S Mulliken’s famous title “What are electrons doing in a molecule?” continues to be relevant. Indeed it was not practically possible to handle the complicated mathematical relations of quantum mechanics and apply them to molecules of moderate size with the desirable chemical accuracy of a kcal unit until recently.

In 1929, Dirac wrote “The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved”. In the early sixties these equations and quantum chemistry (the application of quantum mechanics

to chemical problems) emerged as a new branch of chemistry mainly due to the advent of computers and the corresponding advances in applied mathematics. Over the years this intense multidisciplinary synergy (theoretical and computational development, and the choice of molecular systems) has made chemistry a central discipline in science. There are a large number of specialists drawn from several disciplines who have made this happen.

Walter Kohn and John Pople are the two most prominent figures in this historical process. Kohn's theoretical work has formed the basis for simplifying the mathematics in descriptions of the electronic structure of matter from the perspective of the electronic density, a quantity which is measurable and is close to a chemist's heart. Pople, on the other hand, developed the quantum-chemical methodology from the point of view of Schrödinger's wave function approach. Both of them began to work along these lines with their coworkers in the early sixties. In 1994, Pople finally implemented Kohn's prescription into the most popular computer code called the GAUSSIAN developed and constantly upgraded like the Volkswagen car (it was known in conferences as Pople's Volkswagen ) starting from 1970. Due to these efforts, computer-based calculations are now used routinely to supplement experimental studies and the next generation of chemists may not believe that there existed a distinction between theoretical and experimental chemists in the past. Computer experiments are experiments after all. They are useful too. Several potent drugs in the market today are products of such experiments [1].

As someone who had the privilege of knowing both Kohn and Pople, professionally and personally, I think it is beyond the scope of a single article to cover the scientific profile of these two very creative and successful scientists who have made the post Hartree –Fock era come into existence. A lucid account of John Pople's scientific contributions has been recently published [2]. It may be added here that the contribution of S F Boys from Cambridge, UK, of introduction of the Gaussian functions to

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chemistry probably motivated Pople later on to develop those remarkable basis sets which work like spices in improving the taste (accuracy) of computations. In the present article a brief sketch of the major scientific contributions of Walter Kohn will be presented.

Hulthen–Kohn is the most important method to calculate the phase shifts of scattering theory.

Born on 9 March, 1923, in Vienna, to Jewish parents, Walter Kohn went to school in England. He obtained his BA from the University of Toronto in 1945, majoring in Mathematics and Physics. After completing MA in applied mathematics from Toronto in 1946, he joined Harvard University to work for a PhD degree under Julian Schwinger (Nobel Laureate, 1965) famous for his monumental relativistically covariant renormalization theory of quantum electrodynamics; quantum gauge theories). Walter Kohn has been one of the early graduate and postdoctoral students of Julian Schwinger and he recollects [3] “*And what did I carry away with me from my two years with Schwinger as his graduate student and two years as his postdoc? The self-admonition to try and measure up to his high standards; to dig for the essential; to pay attention to the experimental facts; to try to say something precise and operationally meaningful, even if – as is usual – one cannot calculate everything a priori; not to be satisfied until one has embedded his ideas in a coherent, logical and aesthetically satisfying structure*”.

Walter Kohn’s contributions towards understanding condensed matter can be gauged from the fact that quite a number of diverse phenomena are named after him. Some of his major contributions are briefly described here.

In the late forties, he designed a variational principle for the scattering amplitude (nuclear scattering theory), which is known as the Hulthen–Kohn variational principle. It is the most important method to calculate the phase shifts of scattering theory.

In the early fifties, inspired by the experimental observations that the optical spectrum of impurity atoms in semiconductors is often well described by the simple Rydberg formula of

hydrogen-like atoms, Kohn developed, from a many-body point of view, the understanding that the electrons captured by an impurity, in spite of their strong interaction with the other electrons approximately satisfy a hydrogen-like Schrodinger equation. The bare electron mass in this equation is replaced by an effective mass and the bare coulomb potential is reduced by the dielectric constant of the medium. In semiconductor physics, this is the so-called 'effective-mass theory'.

In 1954, Walter Kohn, in collaboration with N Rostoker, developed a Green-function method to calculate the band structure of solids. Popularly known as the KKR method (Korringa–Kohn–Rostoker method), it is the most important numerical scheme for calculating band structures of solids.

Around 1957, Walter Kohn got interested in describing the Bloch electrons in strong magnetic fields. The Kohn theory proves that electrons in an external magnetic field, in spite of their mutual interaction, yield a simple oscillator spectrum. This theorem in its generalizations has been recently applied with success to describe quantum dots and quantum wires in strong magnetic fields.

In 1959, Walter Kohn discovered that the Fermi-surface singularity of the dielectric function must lead to 'kinks' in the phonon spectrum of metals. Known as the Kohn anomaly, this theoretical prediction was experimentally verified 8 years later!

In the early sixties, working together with J M Luttinger, Walter Kohn discovered the so-called anomalous diagrams in the many-body perturbation theory as applied to solids. These are the Feynman diagrams of the *finite*-temperature formalism, which in the zero temperature limit, do not become zero, although the corresponding diagram of the *zero*-temperature and perturbation formalism do become zero. These anomalous diagrams lead to a total energy lower than that of the zero temperature formalism. In 1965, again with Luttinger, he predicted that the electron gas with its purely repulsive Coulomb interaction becomes

The Kohn theory proves that electrons in an external magnetic field, in spite of their mutual interaction, yield a simple oscillator spectrum.

superconducting at sufficiently low temperatures. This was also one of the pioneering theoretical works leading to non-phononic superconductivity, exhibited by the materials now known as the high  $T_c$ -superconductors.

In 1964, Kohn got interested in the description of inhomogeneous electron systems. The common examples of such systems are atoms, molecules, clusters, solids and surfaces – the real chemical systems. Together with Pierre Hohenberg, he proved the Hohenberg–Kohn theorem [4], which provides the foundation of the density functional theory. According to this theorem, the knowledge of the ground state density is sufficient to determine all observable quantities of a stationary nondegenerate system, including the energy. The complicated inter-electronic repulsion effects (exchange and Coulomb correlation effects) which become a bottleneck in the traditional wave functional theories are simplified within the density functional theory, since the average electron density – a much simpler quantity – is used to describe the correlated motion of the electrons. The computational advantage in the reduction of the dimensionality of the problem (from  $3N$  to 3) has made the density functional theory a favorite of all quantum chemists as realistic chemical systems can be actually computed – faster and more accurately.

The Kohn–Sham equations look like the good old Hartree-equations making calculations of large molecules far easier.

In 1965, Kohn and Sham derived [5] the celebrated Kohn–Sham equations, which provided the computational framework for the series of approximate density functional theories, which took birth during the following decades. Kohn–Sham theory prescribes how to calculate the ground-state density of the fully interacting system from the so called Kohn–Sham *orbitals* of non-interacting particles moving in an effective local single particle potential. What is more, the Kohn–Sham equations look like the good old Hartree-equations making calculations of large molecules far easier. With the availability of supercomputers and efficient algorithm developments, the equilibrium configurations of systems with thousand atoms (pseudopotentials, Car–Parrinello molecular dynamics simulations [6]) can be studied within the Kohn–Sham approximation with reliable

accuracy. The order  $N$ -calculations, the dream of theoretical chemists, in which the computations scale linearly with the number of atoms could be realized very soon. It may be noted here that the coupling parameter of the Kohn–Sham formalism is a hot area of research today and the adiabatic connection methods, defined as the path over which the density is held fixed as the electron–electron coupling changes from zero to one, holds the possibilities of very interesting future developments in the density functional theory.

In the seventies, Kohn and Lang applied the Kohn–Sham method to metal surfaces and also studied the surface chemisorption. In the eighties and nineties, Kohn generalized the density functional theory to degenerate ground states, excited states (limited), time dependent systems, superconductors and also treated the elusive van der Waals forces using this theory.

This is the scientific profile of the person who is the product of the most fascinating era of physics at Harvard about which he recollects [3]—*“In one corner, at a desk, sat Harold Levine calculating away on intricate classical wave problems, totally oblivious to what was going on around him. Drifting in and out were other students anxious to catch Julian. Frequently, Herman Feshbach came over from MIT to talk about nuclear forces. A few times Freeman Dyson and Richard Feynman dropped in to talk about quantum electrodynamics. Once a letter or preprint from Tomonaga arrived and Julian said he was nervous to open it, so often had Tomonaga’s thinking been almost the same as his. What great fortune for us to be there at such a time !”*

Kohn was honored with Oliver–Buckley Prize of the American Physical Society in 1960 for his early contributions to the development of solid state physics. In 1977, he was awarded the Davison–Germer Prize, APS for his contributions to surface physics. In 1991, he received the Eugene–Feenberg Medal for his total contribution to the development of density functional theory.

Walter Kohn founded the Institute for Theoretical Physics at the University of California, Santa Barbara in 1979. Today, this

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Institute is a leading international research and training center in condensed matter science. He is also the co-founder of the 'Santa Barbara Institute of Global Conflict and Cooperation'. One of the principal aims of this Institute is to create public awareness and opposition against the 'Star Wars' program of President Ronald Reagan.

V Ambegaokar (Cornell), Vachaspati (Allahabad), CK Majumdar and Amitava Bagchi (both Calcutta) have been the Indian graduate students of Kohn [6–9]. In January 1995, Kohn visited India with A K Rajagopal and was highly appreciative of the fundamental science done from India.

Walter Kohn has three daughters from his first wife, Lois Kohn. "My daughters would love to wear them" he remarked at Charminar's Churi Bazar in Hyderabad in January 1995. Kohn now lives with his second wife, Mara Kohn in Santa Barbara.

In 1995, I wrote to him mentioning his striking resemblance in looks with Mother Teresa. Indeed, both have made impossible things possible with extraordinary simplicity and complete dedication to the purpose. Incidentally, Walter Kohn very recently wrote to me that these days he is reading chemistry textbooks like mad!

### Acknowledgements

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### Suggested Reading

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Pauli's whole character was different from mine. He was much more critical and he tried to do two things at once while I would think that this is really too difficult for even the best physicist. He tried first of all to be inspired by the experiments and to see in a kind of intuitive way how things are connected, and at the same time he tried to rationalize his intuitions and to find a rigorous mathematical scheme so that he really could prove anything what he said. Now this is, I think, simply too much, and therefore Pauli has through his whole life published much less than he could have published if he had abandoned one of these two postulates. Bohr had dared to publish papers which he could not prove and which were right after all. Others have done a lot by rational methods and by good mathematics, but the two things together that I think is too much for one man.

*Werner Heisenberg*

Like Heisenberg, Pauli was the well-bred son of a university professor, and in their personalities they had much in common. Both were sensitive, naïve, adolescent, personally insecure but academically confident, enormously ambitious, and thoroughly dedicated to theoretical physics. The similarities ended there. Outwardly, Heisenberg was quiet and friendly, at once retiring and almost recklessly daring – in life and in science – while Pauli was outspoken, aggressive, carefully systematic, and often devastatingly critical.

*David Cassidy*

