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Title

Obituary for Walter Kohn (1923–2016)

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Walter Kohn (Figure 1) is one of the most cited scientists of our time, who died on 19 April 2016 in Santa Barbara, CA, USA. He was an outstanding scientist with a life story from tragedies to highlights. Walter was born in Vienna on 9 March 1923 into a Jewish family. As a child, he attended the renowned Academic Gymnasium, where he liked Latin the most, but had little interest in physics or mathematics. The situation changed drastically in 1938 when Austria joined Nazi Germany—*the Anschluss*—and Walter was forced to leave this gymnasium, but he was able to enroll in the Jewish Chajes Gymnasium. There were two teachers—especially Emil Nohel, a former assistant of Einstein—who initiated his ambition for physics and mathematics. In 1939, the Kohn parents sent their 16-year-old son to Great Britain with one of the last children's transport rescue missions (*Kindertransporte*). Walter never saw his parents again, as they were killed in Auschwitz. In 1940, when there was a risk of a UK invasion by Germany, he and other men who held German passports were considered to be "enemy aliens" and put in detention camps: first on the Isle of Man, and then Walter was shipped to Canada, where he worked in a woodcutter camp.

He started his scientific career in Toronto, where he (as an "enemy alien") was not allowed to enter the chemistry building; thus, he studied physics and mathematics, finishing with a master's degree. In 1946, he moved to Harvard. As Walter mentioned later on, he was asked by John Van Vleck (department chairperson) to work in his Ph.D. thesis on band theory and solid-state physics, but he refused and went to the young Julian Schwinger, an expert in variational methods, who became his Ph.D. adviser. The topic was quantum-mechanical description of the collision of light nuclei. In 1948, he received his Ph.D. in theoretical physics. Now Van Fleck (who went for a sabbatical) asked Walter to teach his course in solid-state physics, which became a focus in Walter's scientific life. Other important factors that contributed to the choice of his research were a postdoctoral study at the Niels Bohr Institute in Copenhagen, a consultancy for the Bell Telephone Laboratories, where he did most influential research work with Joaquin Luttinger, and teaching at the Pittsburgh Carnegie Institute of Technology (now Carnegie Mellon University). There, he developed his theory on anomalies in the phonon spectra of metals, now known as the Kohn anomalies. In his scientific carrier, he was active at many places, including Pennsylvania, Michigan, Washington (Seattle), Paris, Imperial College (London), and the ETH (Zürich). In 1957, he became an American citizen, and in 1960, a professor at the University of California, San Diego, where he was chairman of the Physics Department for three years. In 1979, Walter became the founding director of the Institute for Theoretical Physics at the University of California, Santa Barbara, (today's Kavli Institute for Theoretical Physics), where he was director until 1984.

Figure 1. Walter Kohn was presented receiving an honorary Doctor of Science degree by the Harvard University (AP Photo/Steven Senne).

In 1998, he (together with John Pople) was awarded the Nobel Prize in Chemistry (not in physics) for his pioneering scientific contributions. In this context, Walter told with irony, that he as a student had never taken a single course in chemistry. In addition, Walter has received multiple honors and honorary Doctors degrees: University of Toronto (1967), Universite de Paris-Sud (1980), Hebrew University of Jerusalem (1981), Brandeis University Boston (1981), Queen's University Kingston (1986), ETH Zürich (1994), Universität Würzburg (1995), Technische Universität Wien (1966), Weizmann Institute (1997), Tel Aviv University (1999), Carnegie Mellon University (1999), Rutgers University (2001), Oxford University (2001), University of Sherbrooke (2002), TU Dresden (2002), Freie Universität Berlin (2003), Universität Wien (2012), and Harvard University (2012).

The special honors that Walter Kohn received illustrate his interdisciplinary approach in science: Oliver Buckley Prize (Solid State Physics, 1960), Davisson–Germer Prize (Surface Physics, 1977), National Medal of Science, USA (1988), Feenberg Medal (Many Body Physics, 1991), Niels Bohr/UNESCO Gold Medal (1991), Harvard University, (Centennial Medal, 2001), Ecole Normal Superieure, Les Trois Physiciens (2003), Richard Prange Prize (2010).

With respect to Walter's ambivalent relation to Austria, emphasizing that Austria did not learn enough from its Nazi past, it is appropriate to mention that he also received additional honors in Austria; namely, in 1999, the Special Award for Science and Art (*Österreichisches Ehrenzeichen für Wissenschaft und Kunst*) and in 2009, the Great Silver Award for the Republic of Austria (*Großes Silbernes Ehrenzeichen um die Republik Österreich*). In 2011, he became an honorary member of the Austrian Academy of Science.

Walter received the Nobel Prize for the development of density functional theory (DFT), and thus it is appropriate to mention the crucial steps in a historical fashion. We need a quantum mechanical treatment to describe the electronic structure of a system (at the atomic scale) and solve a many-particle Schrödinger equation, a task that is intractable. With the Born–Oppenheimer approximation, one can start with the time-independent Schrödinger equation, and describe each electronic state by a many-electron wave function (WF). An alternative route to the direct solution of Schrödinger's equation is shifting the focus from the wave-function-based theory to the fundamental observable of the problem, namely the electron density $\rho(\mathbf{r})$. There are two classes of electronic structure methods: wave-function-based and density-based schemes, both of which have their advantages and disadvantages.

In the nineteen fifties and sixties, computation of the electronic energy structures generally fell into two separate camps: one was very accurate in the results of an independent electron in a constructed "effective" potential, and the other applied the then-flourishing many-body theory to compute the interaction effects in a totally flat potential landscape. In the mid-sixties, the density functional theory combined the fruits of both schools by a revolutionary view, reversing the traditional roles of the potential landscape vis-à-vis the electron density distribution as cause and effect. The change was the fruit of the persistent study of Kohn on electron density. He started at the Carnegie Institute of Technology with his student, Seymour Vosko (1960), examining the change of the spatial distribution of the electron density when an impurity is added to a metal. The wave-like density—known as the Friedel oscillations—reflects the quantum nature of the energy boundary that separates the states occupied by electrons, and those unoccupied. Kohn felt for a number of years that there was something more to the density distribution than just its mundane definition. He found, for example, the Friedel signature in the vibration frequency spectrum of a metallic lattice from the electron contribution, known as the Kohn anomaly. He and Luttinger had a theory that these oscillations caused the normal metal state to be unstable in extremely low temperatures, when it became a superconductor. Such deep enquiries led in 1964 to the establishment of the famous Hohenberg–Kohn theorem basis of DFT, which proved that the electron density serves as the determinant of the properties of a many-electron system, in place of the potential provided by the charge of the nuclei (i.e., the electrostatic energy landscape).

In contrast to the wave function-based methods, the fundamental idea of density functional theory is to replace the complete many-electron wave function with the much simpler ground-state electron density as the main variable. In 1963, Walter spent a sabbatical semester at the École Normale Supérieur in Paris, where he, together with Pierre Hohenberg, laid the basis for DFT; namely, the Hohenberg and Kohn [1] principle, published in 1964. For any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, the ground-state density is uniquely determined. In this formulation of DFT, they demonstrated a unique one-to-one mapping between the external potential $V_{ext}(\mathbf{r})$ (from the nuclei) applied to a nondegenerate electronic system and its ground state density $\rho(\mathbf{r})$, which depends on the position $\mathbf{r}$ (i.e., only three coordinates). This mapping implies that the ground state energy E of the system is a functional of its ground states density $\rho(\mathbf{r})$. The Thomas–Fermi model of 1927 already had a similar goal, but was a severe approximation insufficient for chemical accuracy. The fundamental work by Hohenberg and Kohn showed that a universal functional for the energy $E[\rho(\mathbf{r})]$ can be defined in terms of the density. The exact ground state is the global minimum value of this functional. In principle, this formulation is exact; however, since the explicit mathematical form is unknown, one does not fully know how to express the interaction between individual electrons, making approximations necessary.

A year later, Walter returned to San Diego, where he and Lu Jeu Sham proposed a scheme to make DFT calculations feasible, now called Kohn–Sham (KS) equations [2]. Their main idea is that the density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles, the "KS electrons". Their KS orbitals represent the density. Kohn and Sham introduced the KS equations with a local one-body potential—the KS potential—mimicking all inter-electronic interactions via Hartree and exchange-correlation contributions representing the

many-body nature. One of the reasons for the much higher accuracy is that the kinetic energy (a large fraction of the total energy) can be computed with high numerical precision when orbitals are available, in contrast to the Thomas–Fermi scheme. What counts at the end are energy differences, and what survives determines physics. Let us take Si as an example: the total energy difference between the rocksalt and zinkblende structure is just 0.014% of the energy of a Si atom. In terms of the total energy, the exchange and correlation part is only a small contribution, and thus approximations make sense; however, for various properties, they may well be crucial.

Kohn and Sham expressed skepticism in their first paper about applying the density functional theory to chemical bonding, because it occurred at the low-density region, not in the realm of validity of higher densities examined by a field theoretic analysis in 1965 with Sham focusing on the many-electron solid state system. This aspect about chemical binding is surprising, since the Kohn–Sham paper [2] was the main reason for the Nobel Prize in Chemistry. These two papers [1,2] are often cited in computational physics and chemistry.

Nowadays, computational chemistry and physics is often done within density functional theory, which occurs in a large variety of approximations. They need to be explored and validated by even more sophisticated methods, which may be limited by the computational effort for large system sizes. The interdisciplinary nature of these issues is obvious, since the open challenges include chemistry, physics, mathematics, computer science, biology, and materials science. By a combined effort of experts from all these fields, a substantial process has been achieved. The significant impact DFT had for studying solids become apparent from a recent study, in which 40 different DFT codes were analyzed for reproducibility and verification, as documented in [3].

As the numerical schemes used in solving the Kohn–Sham equations were shown to be equivalent in this study, the remaining difference in results between different studies involving the same material is due to the choice of the exchange-correlation density functional. The local-density approximation is very similar to the $X\alpha$ method of Slater, but differs in its motivation; namely, that it is the remaining contribution to the energy when all known density functional contributions are subtracted from the exact uniform electron gas energy calculated with an accurate Schrödinger equation-based method. The success of exchange-correlation functionals used for chemistry systems—and the reason the Nobel Prize was awarded in Chemistry—is based on the availability of accurate Schrödinger equations solutions for a large number of atoms and molecules that can be used in the construction of accurate exchange correlation functionals for a wide variety of chemical situations and systems. While the availability of exact solutions for solid-state systems is far more restricted, the local density approximation has served much better than expected. Walter had an interest in expanding upon the local-density approximation by considering additional paradigm systems to the uniform electron gas.

Walter was often the keynote speaker at the many DFT biennial meetings, which took place in Paris (1995), Vienna (1997), Rome (1999), Madrid (2001), Brussels (2003), Geneva (2005), Amsterdam (2007), Lyon (2009), Athens (2011), Durham (2013), and Debrecen (2015). The last one he attended was in Athens, where he gave a talk on "Nearsightedness of electronic matter". Here he illustrated his interdisciplinary nature. For a given material (especially an insulator), one would say in chemistry that an atom interacts strongly only with its nearest neighbors, which means in physics that the Hamilton matrix has only large values near the diagonal (atoms). Neglecting the small interactions leads to a band matrix, for which the mathematicians know that its diagonalization scales linearly with N—the number of atoms—(in contrast to a full Hamiltonian scaling with N^3), nowadays called "order-N method". In terms of applications, this means that larger systems (which are a more realistic representation of a real material) can be studied. In this talk, he made the bridge from chemistry to applications. Not only was his talk in Athens impressive, but so too was the fact that he joined the participants to visit the Acropolis in the age of 88 years (Figure 2).

Figure 2. Walter Kohn at the excursion to Acropolis during the density functional theory (DFT) conference held in Athens in 2011.

Walter Kohn was not only one of the most prominent scientists of his time, but was interested and active in many fields, such as art, literature, history, humanities, and environmental issues; we mention as just one example that he was executive producer of the 2005 film *The Power of the Sun* (http:/powerofthesun.ucsb.edu). All colleagues will keep him in loving memory, due to his creative and critical thinking. He is deeply missed by his many friends.

Conflicts of Interest: The authors declare no conflict of interest.

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