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## The education of Walter Kohn and the creation of density functional theory

Andrew Zangwill

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**Abstract** The theoretical solid-state physicist Walter Kohn was awarded one-half of the 1998 Nobel Prize in Chemistry for his mid-1960s creation of an approach to the many-particle problem in quantum mechanics called density functional theory (DFT). In its exact form, DFT establishes that the total charge density of any system of electrons and nuclei provides all the information needed for a complete description of that system. This was a breakthrough for the study of atoms, molecules, gases, liquids, and solids. Before DFT, it was thought that knowledge of the vastly more complicated many-electron wave function was essential for a complete description of such systems. Today, 50 years after its introduction, DFT (in one of its approximate forms) is the method of choice used by most scientists to calculate the physical properties of materials of all kinds. In this paper, I present a biographical essay of Kohn's educational experiences and professional career up to and including the creation of DFT. My account begins with Kohn's student years in Austria, England, and Canada during World War II and continues with his graduate and postgraduate training at Harvard University and Niels Bohr's Institute for Theoretical Physics in Copenhagen. I then study the research choices he made during the first 10 years of his career (when he was a faculty member at the Carnegie Institute of Technology and a frequent visitor to the Bell Telephone Laboratories) in the context of the theoretical solid-state physics agenda of the late 1950s and early 1960s. Subsequent sections discuss his move to the University of California, San Diego, identify the research issue which led directly to DFT, and analyze the two foundational papers of the theory. The paper concludes with an explanation of how the chemists came to award “their” Nobel Prize to the physicist

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Kohn and a discussion of why he was unusually well suited to create the theory in the first place.

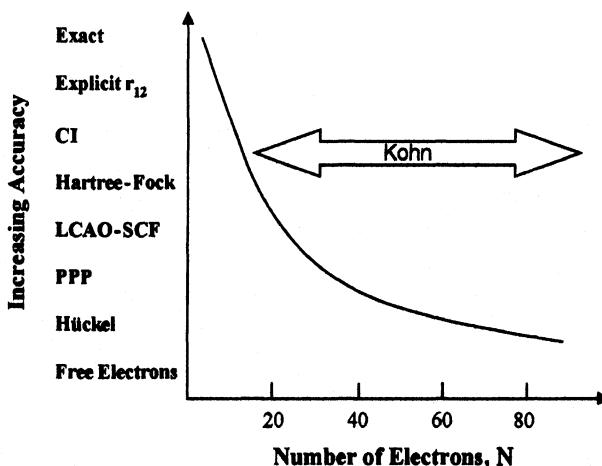
## 1 Introduction

The 1998 Nobel Prize in Chemistry recognized the field of quantum chemistry, a theoretical enterprise where quantum mechanics is used to study molecules and address chemical problems (Barden and Schaeffer 2000; Gavroglu and Simões 2012). The prize was shared equally by “Walter Kohn for his development of density functional theory and John Pople for his development of computational methods in quantum chemistry” (NPC). The award to Pople surprised no one. Ten years earlier, an international conference, “Forty Years of Quantum Chemistry,” had honored Pople’s career-long commitment to developing semiempirical and first-principles methods to predict the structure and properties of molecular systems (Handy and Schaefer 1990). A notable early contribution was the 1970 free release of his group’s GAUSSIAN computer program which solved the Schrödinger equation for molecules in the Hartree-Fock approximation. Today, after decades of improvements in accuracy and functionality, it is estimated that 90 % of all quantum chemistry calculations are performed using the (now commercial) GAUSSIAN suite of programs (Crawford et al. 2001).

By contrast, the fact that Walter Kohn earned a share of the Nobel Prize in *chemistry* surprised many because his international reputation was gained as a theoretical solid-state physicist. Indeed, his body of work had previously earned him the Oliver E. Buckley Prize (1961) and the Davisson–Germer Prize (1977) of the American Physical Society for his contributions to, respectively, “the foundations of the electron theory of solids” and “understanding the inhomogeneous electron gas and its application to electronic phenomena at surfaces”.<sup>1</sup> A card-carrying chemist could reasonably ask: what do these things have to do with quantum chemistry? The answer lies in the research Kohn conducted in the period 1963–1965 which created the density functional theory (DFT) cited by the Nobel committee. This theory focuses on the density of electrons in an atom, molecule, or solid rather than on the many-electron wave function, which is the central concern of traditional quantum chemistry.

The connection between the work of the two 1998 Chemistry Nobel Laureates can be understood from the “hyperbola of quantum chemistry” which Pople published in the proceedings of a 1965 symposium on atomic and molecular quantum theory (Pople 1965; Park 2003). The horizontal axis of this graph (see Fig. 1) indicates the number of electrons  $N$  in the system of interest. The vertical axis lists a sequence of quantum mechanical methods (in order of increasing accuracy) used to determine the system’s “electronic structure,” i.e., its many-electron wave function, electronic charge density, electron energy levels, and other properties calculable from these. Pople suggested that the activities of most quantum chemists tended to cluster around the extremities of the hyperbolic solid line. Those interested in the highest accuracy were forced by computational constraints to focus on small molecules (small  $N$ ) while those interested in large molecules (large  $N$ ) were forced by computational constraints to use methods

<sup>1</sup> Prizes of the American Physical Society (AMP).



**Fig. 1** The applicability range of Kohn's density functional theory placed on Pople's hyperbola of quantum chemistry. Adapted from Pople (1965)

that were capable of only low accuracy. He noted that progress would occur by moving off the hyperbola either horizontally from left to right or vertically from bottom to top.

The density functional theory created by Walter Kohn represented a dramatic move away from Pople's hyperbola, particularly for systems with a large number of electrons (see the arrow in Fig. 1). Many chemists were wary (or dismissive) of this theory at first because it made no use of the  $N$ -electron wave function, a quantity thought to be indispensable for a proper description of any atom or molecule. Eventually, improvements to Kohn's theory made by chemists themselves led to quantitative successes that could not be denied. Today, it is the method of choice used by most scientists who wish to calculate the properties of real materials.

Unlike many other scientific achievements, the technical question which led Kohn to create DFT in the mid-1960s was not "in the air" among physicists, chemists, or anyone else. It is entirely possible that the theory would be unknown today if Kohn's background, technical skills, and scientific experiences differed very much from what they were. Accordingly, this article (1) recounts the unusual personal and intellectual journey which led to Walter Kohn's success as a theoretical physicist; (2) identifies the scientific issue which motivated the creation of DFT in the context of theoretical solid-state physics research in the 1960s; (3) summarizes the key elements of the founding papers of DFT; (4) argues that Kohn's scientific background made him particularly well suited to create density functional theory; and (5) explains in brief how Kohn came to win a share of the Nobel Prize in Chemistry for the creation of DFT.

## 2 An unsentimental education

In 1933, 10-year-old Walther Kohn<sup>2</sup> began the 8-year course of study at the Akademische Gymnasium, the oldest and one of the best secondary schools in his home city

<sup>2</sup> Walther Kohn began to use the name Walter Kohn informally in 1940 and professionally in 1945.

of Vienna. In doing so, he was not unlike the children of many middle-class Jewish parents who were actively engaged in the intellectual and artistic life of their city.<sup>3</sup> His father Salomon owned an art publishing company that specialized in the manufacture and distribution of high-quality art postcards. His mother Gittel was a highly educated woman who spoke four languages and it was she who chose the humanistically oriented Akademische Gymnasium to educate her son. Walther excelled at Latin and ancient Roman history but showed no apparent aptitude for mathematics. The only grade of C he ever received was in that subject (WK98).

Besides marking the beginning of Kohn's secondary school education, 1933 was also the year that Adolf Hitler and his Nazi party took power in neighboring Germany. The Nazi party was illegal in Austria, but its many sympathizers worked tirelessly to undermine the existing democratically elected government. Finally, in May 1934, the country succumbed to a form of authoritarian rule known to historians as Austro-fascism (Berkley 1988). Four years later, cheering crowds welcomed Hitler when the German army crossed the border and marched into Vienna. The immediately subsequent events were vivid in Kohn's memory many years later (WK98, WK13a):

The family business was confiscated but my father was required to continue its management without any compensation...He wrote to a London art distributor and business client named Charles Hauff (whom he had never met) and asked if he and his wife would temporarily accept me and my older sister Minna into their home. Hauff replied affirmatively and Minna emigrated to England very soon thereafter. For reasons of their own, the Nazis made it much more difficult for young Jewish boys to leave. I remained in Vienna, but was expelled from my school.

Many expelled students never went to school again. Kohn was lucky because he was permitted to finish the school year at a segregated high school for Jews. In August 1938, he was one of a few hundred high-achieving Jewish students from the various Viennese secondary schools who were given the opportunity to continue their education at the Zwi Perez Chajes Gymnasium, a private all-Jewish high school.<sup>4</sup> This experience was transformative for Kohn because his interest in science was ignited by the physics teacher Emil Nohel<sup>5</sup> (Fig. 2) and the mathematics teacher Victor Sabbath. He later recalled that (Kohn 2004, WK00a).

<sup>3</sup> Beller (1989) paints a cultural portrait of the Jewish community in early twentieth century Vienna.

<sup>4</sup> This would be Kohn's sixth (and last) year of secondary school in Vienna. Quite unusually for Austria at that time, boys and girls were not separated for instruction in Walther's small class at the Chajes school (Neuhaus 2003).

<sup>5</sup> Emil Eliezer Nohel grew up on a small farm in Bohemia. He studied mathematics at the Karl-Ferdinand (German) University in Prague and served as an assistant to Albert Einstein when Einstein was a professor there from 1911 to 1914. Nohel's descriptions of the difficult conditions endured by Jews in Bohemia awakened Einstein's concern for the plight of his coreligionists. For most of his career, Nohel taught mathematics at the Handelsakademie Wien, a business-oriented secondary school in Vienna. The Anschluss precipitated his dismissal, and he found work as the physics teacher (and then the principal) of the Zwi Perez Chajes Gymnasium. Nohel was arrested on December 12, 1942, and spent 2 years at the Theresienstadt labor camp before he was transferred to the Auschwitz concentration camp and murdered by the Nazis (Frank 1947; Pais 1982).

**Fig. 2** Emil Eliezer Nohel (ca. 1938) was a high school physics teacher who inspired Kohn to become a scientist. Courtesy of the Yad Vashem Photo Archive



Nohel was a tall, quiet, noble man who devoted himself to his students. It was really a combination of my admiration for this man as a person and his deep knowledge of physics that started me off... Though I was only fifteen going on 16 years old, I already understood—due to Nohel's role model and by comparing myself to others—what it meant to really comprehend something in physics. This is one of the most important insights for a future theoretical physicist.

Sabbath was also a fantastic guy. The thing I remember about him is that while he was teaching us he told us about a new book he was reading by the great French physicist [Louis] de Broglie called *Matter and Light*... Sabbath was a teacher with great enthusiasm and it was very exciting what he told us.

November 10, 1938, was particularly memorable at the Chajes school because it was the day following a night of state-sanctioned destructive violence against Jewish homes, businesses, synagogues, and people. This November pogrom<sup>6</sup> put emigration into everyone's mind, but it was difficult and expensive to make it happen (Ehrlich 2003). Kohn was again lucky. Just 3 weeks before Germany invaded Poland to launch World War II, he escaped probable extermination by the Nazis by virtue of the *Kindertransport*, an organized effort to evacuate Jewish children under the age of 18 from Germany, Austria, and Czechoslovakia. Kohn was one of the 10,000 unaccompanied children who escaped to England between December 1, 1938, and September 1, 1939 (Curio 2004; Fast 2011).<sup>7</sup>

<sup>6</sup> The November pogrom is often called *Kristallnacht* (the night of broken glass), a name coined by the Nazis themselves.

<sup>7</sup> Kohn's parents were murdered by the Nazis in 1944.

By pre-arrangement, Walther went to live with Charles and Eva Hauff, the same couple who had previously welcomed his sister Minna (WK13a). It was also pre-arranged that Kohn should learn to be a farmer, an occupation that would make him less subject to economic dislocations (WK98). Thus, Kohn's formal English education began at a training farm in Kent, where he promptly contracted meningitis. Sulfa drugs saved his life, but left him so weak that going back to the farm was out of the question (WK00a). Luckily, the Hauff's succeeded to enroll Walther in the nearby East Grinstead County Grammar School for the term beginning January 1940. The headmaster, Thomas W. Scott, noted Kohn's poor English skills and created a daily German class where Walther was the only student. The instructor taught English to Kohn for half the class, and Kohn taught advanced German to the instructor for the other half (JF13, WK00b).

Kohn's preparation in mathematics and science was equal to or exceeded that of his fellow 16-year-old English classmates (WK13a). The level of physics he was exposed to at East Grinstead can be judged from two of his textbooks, both intended for students preparing for University Scholarship Examinations. *Heat* (1939) by R.G. Mitton is a thorough introduction to the thermal properties of matter, the kinetic theory of gases, heat engines, entropy, and the laws of thermodynamics. The prose is brisk, yet clear, and the author assumes familiarity with the laws of algebra and the geometrical meaning of the derivative. The oddly named *Properties of Matter* (1937) by D.N. Shorthose is a textbook of particle and continuum mechanics which includes chapters devoted to ballistic motion, circular motion, simple harmonic motion, rigid body motion, hydrostatics, friction, elasticity, and viscosity. The exposition moves freely between geometrical and algebraic reasoning, and the reader is expected to understand first derivatives, second derivatives, and the law of integration which connects them.

Kohn studied at East Grinstead for five months before Germany invaded Holland, Belgium, and Luxembourg on May 10, 1940. Winston Churchill replaced Neville Chamberlain as Prime Minister of Great Britain, and the British newspapers became filled with war hysteria. The British War Office feared that an invasion was imminent and recommended to the Home Office that the government "intern all enemy aliens in areas where German parachute troops are likely to land" (Gilman and Gilman 1980). Arrests begin immediately, and, when Italy entered the war on June 10, Churchill demanded that police officials "collar the lot". This terse order expanded internment to all parts of the country and to all enemy aliens, i.e., to all holders of passports from Italy or Nazi-occupied countries age 17 or older. It took Scotland Yard less than 6 weeks to intern 24,000 men and 4,000 women (Cesarini and Kushner 1993). Those arrested included not just foreign nationals of quite short residency in England like university students but also highly trained scientists, engineers, doctors, artists, and musicians who had lived in England for many years.<sup>8</sup>

Kohn had turned 17 on March 9 and thus was subject to the order of internment. He was arrested and shipped by train to a large camp that had been hastily constructed in the town of Huyton on the outskirts of Liverpool. It was at Huyton that Walther

<sup>8</sup> Vienna native Otto Frisch was working in the physics laboratory of Prof. Mark Oliphant at the University of Birmingham when the roundup of aliens began. He avoided internment only because his employers made the case that he was engaged in important war work (Frisch 1979).

met and began a lifelong friendship with Josef Eisinger, a boy who had been 1 year behind him at the Akademische Gymnasium in Vienna.<sup>9</sup> A week or so later, both boys were transferred to an internment camp on the Isle of Man. The Hauffs arranged for Walther's East Grinstead teachers to send him his physics textbooks because they were told he would return home soon (KH99). Instead, he spent a month on the Isle of Man where there was no work and little food. He lost 30 pounds.

The burden of warehousing this great mass of civilian internees and the belief that many German prisoners of war would arrive soon led Churchill's government to seek help from the British Commonwealth nations. Accordingly, on July 4, 1940, Kohn and his friend Eisinger found themselves bound for Canada aboard a Polish cruise ship that had been captured by the British and converted to a troop transport (Koch 1980; Auger 2005). By the time, the British government discontinued its policy of internments and deportations in early August 1940, nearly 4,400 civilian internees and 1950 prisoners of war had been relocated to Canada. What the Canadians did not know—because the British did not tell them—was that the majority of the civilian internees were not Nazi sympathizers but Jewish refugees from Nazi barbarism.

Kohn spent the next eighteen months in four different Canadian internment camps. He lived a full year at Camp B, a 15-acre compound built in the heavily wooded Acadia forest twenty miles east of Fredericton, the capital of the province of New Brunswick. A vivid portrait of the camp written by Jones (1988) explains that the internees organized themselves into a highly structured mini-society composed of sixteen distinct groups based on age, education, geography, past friendships, religious practices, and political views. Kohn belonged to a group of academically minded boys between 16 and 20. A different group was populated largely by academics from Cambridge University (graduate students, recent Ph.D.'s, postdoctoral fellows, and junior faculty). Even before the construction of the camp was complete, each group elected a leader and a deputy leader, as well as chairmen for the various departments of the internee camp Cabinet.

The camp's Canadian officials had a clear idea of how the able-bodied internees would spend most of their time: lumberjacking in the forest outside the camp for 20 cents a day. Kohn was not unhappy to do this because the sheer physical labor of chopping trees warded off the Canadian winter cold. However, much more important to him were the many hours he spent at the "camp school" where internees with special technical or academic knowledge offered classes for the benefit of anyone who wanted to learn. Appeals to humanitarian organizations and letters written by the instructors to acquaintances around the world produced donations of textbooks, writing materials, exercise books, blackboards, painting supplies, musical instruments, etc. Two months after it opened in November 1940, the camp library boasted a collection of nearly 1,000 volumes.

The Camp B school was organized by Alfons Rosenberg, a 39-year-old former gymnasium teacher from Berlin. The many Cambridge men in the camp offered their services, and, over time, courses were given in accounting, acting, anthropology, archi-

<sup>9</sup> Eisinger's family smuggled him onto a Kindertransport train out of Vienna after failing to find an official sponsor or a foster family for him in England. He fended for himself, working on a farm in Yorkshire and washing dishes in a hotel in Brighton, until the internment roundup of 1940 (JE13).

ture, art history, astronomy, biology, composition, chemistry, economics, engineering, English, French, geography, German, history, Latin, law, literature, mathematics, music theory, philosophy, physics, physiology, political theory, psychology, sex education, Spanish, and typing. Walther attended a daily physics class offered by Kurt Guggenheimer, a chemical physicist who anticipated the shell model of the nucleus by pointing out similarities in the systematics of the binding energies of molecules and nuclei.<sup>10</sup> He also attended a set theory course taught by Fritz Rothberger, a professional mathematician with a Ph.D. from the University of Vienna.<sup>11</sup>

It is easy to demonstrate that Walther took his classes very seriously. First, he earned all passing marks in June 1941 when Rosenberg arranged for his students to sit (inside the camp) for the nation-wide McGill Junior Matriculation Exam—a necessary step to enter a Canadian university.<sup>12</sup> Second, Kohn took the 20 cents a day he earned lumberjacking and used the “princely sum, carefully saved” to order two books which were sent to him at the camp: *A Course in Pure Mathematics* (1938) by G.H. Hardy and *Introduction to Chemical Physics* (1939) by J.C. Slater (WK98). In an uncanny way, the contents of both books foreshadow the mathematical rigor, taste for foundational issues, and deep interest in the properties of matter that characterize much of this subsequent work.

Hardy and Slater were both first-rate researchers with a strong interest in the pedagogy of their fields. Hardy wrote the first edition of his book in 1908 for the express purpose of making the teaching of mathematics more rigorous at British universities.<sup>13</sup> It was aimed specifically at first-year University students of “scholarship standard,” i.e., the top 10–20 % in ability. The preface to the first edition is explicit: this is “a book for mathematicians: I have nowhere made any attempt to meet the needs of students of engineering or indeed any class of students whose interest are not primarily mathematical”. Thirty years later, in the preface to Kohn’s edition, Hardy remarks that “the

<sup>10</sup> Kurt Martin Guggenheimer (1902–1975) studied chemistry at the University of Munich and physics at the University of Berlin. He earned his Ph.D. in 1933 for work on the ultraviolet absorption spectra of zinc, potassium, and cesium under the direction of Fritz Haber. Guggenheimer pursued postdoctoral work in Paris under the direction of Paul Langevin and published his speculations about nuclei while there. He returned to Munich in 1935 but was arrested in 1938 and spent several months at the Dachau detention center. He emigrated to England and was working at King’s College (Cambridge) when he was interned as an enemy alien. After the war, Guggenheimer worked as a lecturer at the University of Bristol and the University of Glasgow before retiring from academic life in 1967 (Rürup and Schüring 2008; Fernandez 2013).

<sup>11</sup> Fritz Rothberger (1902–2000) was a native of Vienna who graduated from the Akademisches Gymnasium and earned B.S. and Ph.D. degrees in mathematics from the University of Vienna. He came under the influence of Waclaw Sierpinski in Warsaw and began his lifelong work in combinatorial set theory. Rothberger emigrated to England just before the start of World War II, and he was working as a scholar at Trinity College (Cambridge) when he was interned. After the war, he served as a professor on the mathematics faculties of several Canadian universities: Acadia, Fredericton, Laval, and Windsor (Swaminathan 2000).

<sup>12</sup> The subjects tested were English literature, English composition, general history, elementary algebra, elementary geometry, physics, Latin authors, Latin composition, German grammar, German composition, intermediate algebra, intermediate geometry, and trigonometry (GG13).

<sup>13</sup> *A Course in Pure Mathematics* is an elegant and rigorous introduction to mathematical analysis for serious first-year college students. The subject matter includes the notions of limit and convergence applied to series, sequences, functions, derivatives, and integrals. All the main theorems of the calculus of a real variable are discussed, as is the general theory of logarithmic, exponential, and sinusoidal functions.

general plan of the book is unchanged” but “I have inserted a large number of new examples from the papers of the Mathematical Tripos”. Kohn would have learned from his campmates that these “new examples” were drawn from the demanding examinations used by Cambridge University to evaluate its students who hoped to earn a BA degree in mathematics.

The Slater book that Walther bought and read (doubtless cover to cover) was very unusual for its time. The preface states that the author worked hard “to make it intelligible to a reader with a knowledge of calculus and differential equations, but unfamiliar with the more difficult branches of mathematical physics”. For that reason, “the quantum theory used is of a very elementary sort...and it has seemed desirable to omit wave mechanics”. On the other hand, the content is far from elementary. Slater notes that “it is customary to write books either on thermodynamics or on statistical mechanics; this one combines both”. Moreover, “atomic and molecular structure are introduced, together with a discussion of different types of substances, explaining their interatomic forces from quantum theory and their thermal and elastic behavior from our thermodynamic and statistical methods”. All told, the first 100 pages cover “Thermodynamics, Statistical Mechanics, and Kinetic Theory,” the second 200 pages discuss “Gases, Liquids, and Solids,” and the final 200 pages concern themselves with “Atoms, Molecules, and the Structure of Matter”.

At the end of July 1941, Kohn and his friend Josef Eisinger were transferred to Camp A in the southern Quebec town of Farnham, 60 km southeast of Montreal (JE13). Camp A also boasted an excellent internee school, and Kohn was able to think deeply about his schoolwork during the hundreds of hours he spent making camouflage nets in the camp knitting shop (WK13a, Auger 2005). At the end of September 1941, Kohn and a group of other internees were permitted to travel (under guard) to Camp S on St. Helen’s Island in Montreal to sit for McGill University’s Senior Matriculation Examination (Fig. 3). The records show that Kohn did well in all the subjects tested: algebra, geometry, trigonometry, physics, chemistry, and coordinate geometry (GG13).

Opportunity arrived for Kohn and Eisinger in October 1941 when they received a letter from the wife of a faculty member at the University of Toronto. She had

**Fig. 3** Walther Kohn in Canada at age 18 (1941). Courtesy of Josef Eisinger



heard about them from a former internee and offered to sponsor them to come live with her family after their release (Eisinger 2011).<sup>14</sup> Letters were exchanged with Scotland Yard, and, by the end of January 1942, the boys found themselves sharing a comfortable attic space in the home of Hertha and Bruno Mendel.<sup>15</sup> The Mendels were refugees from the Nazis themselves who had earlier helped young Jewish couples escape Germany and start new lives in Canada (Feldberg 1960).<sup>16</sup> Within days, Eisinger was enrolled in a Toronto high school. Kohn, who was 1 year older, needed help from two complete strangers to get started at the University of Toronto.<sup>17</sup> He first received some valuable advice (WK13a),

Dr. Mendel worked at the university and his good friend, Leopold Infeld, came to their home very soon after I arrived. Infeld questioned me about my plans and I told him I wanted to be an engineer (another practical profession). He asked "Is that your main interest?" and I said no, it was mathematics and physics. He told me that engineering at the university was good but that the Math–Physics program was superb and that I should pursue a degree there. With the training I received, I could always do engineering.

At that time, the University of Toronto had a Mathematics Department, a Physics Department, and a small (five-person) Department of Applied Mathematics (de Beau-regard Robinson 1979). Leopold Infeld was a member of the Applied Mathematics faculty, having come to Toronto in 1938 after working with Albert Einstein for 2 years at the Institute for Advanced Study in Princeton.<sup>18</sup> The Math–Physics program recommended to Kohn by Infeld was an honors curriculum where all physics, mathematics, and applied mathematics students took the same courses for the first 2 years and then specialized in their final 2 years (Allin 1981).

<sup>14</sup> The Canadian government announced on May 1941 that any internee under the age of 21 cleared by Scotland Yard would be released and given the opportunity to continue his education in Canada if he could find a sponsor willing to pay a fee of two thousand dollars (Jones 1988).

<sup>15</sup> Eisinger was released in early January. Kohn was released a few weeks later after a short stay at Camp N, an internment camp outside the town of Sherbrooke, Quebec, about 130 km east of Montreal (Eisinger 2011, JE13).

<sup>16</sup> Bruno Mendel (1897–1959) was the son of a research-active medical doctor who trained in Berlin and became a research-active physician himself. His medical practice slowly became less important as he increased the time he spent researching the metabolism of the cancer cell in his small private laboratory. Mendel read the political situation correctly, and he took his wife and three children to Holland when Hitler came to power in 1933. In 1937, he emigrated to Canada and became (at first) an unpaid faculty member at the Banting Institute for Cancer Research of the University of Toronto. He returned to Europe in 1950 to accept a chair in Pharmacology at the University of Amsterdam (Feldberg 1960).

<sup>17</sup> Eisinger followed Kohn to the University of Toronto the following year (JE13).

<sup>18</sup> Leopold Infeld (1898–1968) earned the first Ph.D. in theoretical physics awarded by a Polish university from the Jagellonian University in his native city of Krakow. He taught physics at Jewish high schools for nearly a decade before finding a senior assistantship in theoretical physics at Lwow University. Infeld knew the importance of contacts with foreign physicists and successfully gained 2-year visiting positions with Max Born in Cambridge and Albert Einstein in Princeton. With the latter, he co-authored *The Evolution of Physics*, a popular account of the history of ideas in physics. In 1938, Infeld accepted a position at the University of Toronto where he worked on a variety of theoretical problems in general relativity and cosmology. He returned to Poland in 1950 to found an Institute of Theoretical Physics at the University of Warsaw (Infeld 1978).

**Fig. 4** Dean Samuel Beatty (ca. 1953) bent the admission rules so Kohn could enter the University of Toronto. Courtesy of the University of Toronto Archives



Walther attempted to enroll in Toronto's Math-Physics program, but was rebuffed by the University registrar because he lacked some of the mandatory prerequisites (WK13a). Mendel and Infeld arranged a meeting for Kohn with the Dean of the College of Arts & Science, Samuel Beatty (Fig. 4), who was also the chair of the Mathematics Department.<sup>19</sup> Beatty was sympathetic, but he was unable to move the inflexible registrar. Therefore, he proposed to admit Walther as a "special student" who did not need the prerequisites. This time, it was the chair of the Chemistry Department, Frank Kenrick, who threw up a roadblock by refusing to allow a foreign national from any Triple Axis country to enter his chemistry building where war research was being conducted. Beatty arranged for Kohn to plead his case in person, first with Kenrick (who refused to acknowledge that Kohn was a refugee) and then with the University Chancellor, Rev. Henry John Cody (who was unwilling to overrule one of his department chairs).

In the end, the creative Beatty simple redefined the meaning of "special student" to constitute the normal Math-Physics curriculum minus the usual chemistry requirement. In this way, Kohn entered the Math-Physics program several weeks after the beginning of the spring 1942 term. Relatively, little time was lost because Beatty had permitted Kohn to audit his gateway mathematics course the entire time the admission negotiations were going on. Even after the formalities were completed, Beatty tutored Walther privately for a month to bring him up to speed with the rest of the class.

Kohn's undergraduate transcript shows that he completed the 2-year Math-Physics "common core" in three semesters.<sup>20</sup> Besides algebra, analytic geometry, differential and integral calculus, differential equations, physics laboratory, mechanics, properties of matter, dynamics, electricity & magnetism, and light & acoustics, one finds two required courses in actuarial science, two required courses in French and German

<sup>19</sup> Samuel Beatty (1881–1970) earned the first Ph.D. in mathematics awarded by a Canadian university at the University of Toronto. He remained at Toronto and from 1911 to 1959 rose from Lecturer in Mathematics to Professor and chair of Mathematics, to Dean of the College of Arts & Science, and finally to Chancellor of the entire University (de Beauregard Robinson 1979).

<sup>20</sup> Dean Beatty apparently "regularized" Kohn's "special student" status at some point because his official transcript inaccurately states that he completed an introductory chemistry course and a chemistry laboratory course (CS13).

replaced by English courses, and two elected courses in “oriental literature” where texts in ancient Egyptian, Arabic, Hebrew, Persian, and Turkish were read in translation. Kohn took twelve more advanced courses during the 1943–1944 academic year, including algebraic geometry, differential geometry, partial differential equations, the theory of functions, group theory, thermodynamics, classical dynamics, quantum mechanics, variational principles in physics, English literature, and modern ethics. These two semesters turned out to be his last as an undergraduate because he was inducted into the Canadian army in September 1944.<sup>21</sup> He served until the war ended in August 1945 and was awarded his BA in Applied Mathematics at the summer 1945 convocation ceremony while still on active duty.<sup>22</sup>

The bare list of courses Kohn took during his five undergraduate semesters does not communicate the elite quality of the instructors who taught and mentored him. Leopold Infeld, who lectured to upperclassmen only, had been invited to join the Applied Mathematics Department by its chair, the eminent Irish mathematician and theoretical physicist, J.L. Synge.<sup>23</sup> Synge and his Applied Mathematics colleague Bernard Griffith were the authors of *Principles of Mechanics*, the introductory but quite sophisticated textbook used by all the students in the Math-Physics program. Synge was always eager to add talent to his faculty, and in 1941, he succeeded to recruit the Russian mathematical physicist Alexander Weinstein, a mature scientist with a strong reputation for his work on free boundary problems and variational principles.<sup>24</sup>

It is significant to our story that variational methods were something of a Toronto speciality at the time. Besides Weinstein, Synge, and Griffith, one should include Gilbert Robinson (Mathematics) and Arthur Stevenson (Applied Mathematics) because Cornelius Lanczos thanks them in the preface to his now-classic 1949 text *The Variational Principles of Mechanics* because they together “revised the entire manuscript”. In later years, Kohn singled out the algebraist Richard Brauer and the

<sup>21</sup> Kohn and Josef Eisinger had volunteered for (and been rebuffed by) the Canadian Air Force immediately after their release from internment (JE13).

<sup>22</sup> Kohn worked the summers of 1942–1943 for the Sutton-Horsley Company, a Toronto X-ray equipment manufacturer which began producing signalling lamps and instrument panels for fighter and bomber aircraft after the war began. His specific task was the design and testing of compensation circuits to ensure that cockpit instruments gave accurate readings when operated at unusually high and low temperatures. Kohn worked the summers of 1945–1946 for the mineral surveying and exploration geophysics company Koulomzine, Geoffroy, Brossard & Company of Val D’Or, Quebec. His job was to conduct magnetic field surveys in suspected gold-bearing regions of northern Ontario. A typical survey consisted of a grid of about 1,000 magnetometer measurements with a grid spacing of 100 m (GFF46, WK98, WK13b, HF13).

<sup>23</sup> John Lighton Synge (1897–1995) studied mathematics at Trinity College Dublin and accepted a position as Assistant Professor at the University of Toronto in 1920. There he began a lifelong interest in Einstein’s theory of relativity and in geometrical methods to analyze dynamical systems. The peripatetic Synge subsequently held positions in Dublin, Toronto (again at the time Kohn was there), Ohio State, Carnegie Tech, and finally the Dublin Institute for Advanced Studies (Florides 2008).

<sup>24</sup> Alexander Weinstein (1897–1979) was a Ph.D. student of Hermann Weyl. He worked with Tullio Levi-Civita in Rome and Jacques Hadamard in Paris before the German occupation of France in 1940 drove him from Europe permanently. Weinstein was a member of the Applied Mathematics faculty of the University of Toronto from 1941 to 1946, worked for some time at the US Naval Ordnance Laboratory, and spent 18 productive years at the Institute for Fluid Dynamics and Applied Mathematics at the University of Maryland (Diaz 1978).

non-Euclidean geometer H.S.M. (Donald) Coxeter as “luminous faculty members whom I recall with special vividness” (WK98). He also recalled the first-year electricity and magnetism lectures given by Lachlan Gilchrist, a 1913 Ph.D. student of Robert Millikan, because Gilchrist told his Toronto students that it was he who had purchased the oil used by Millikan in his famous oil drop experiment (WK03).

Weinstein’s influence on the undergraduate Kohn is apparent from Walter’s first two published scientific papers.<sup>25</sup> The first, submitted in July 1944, is a two-page report on an exact solution for the oscillations of a spherical gyroscope which generalizes a method presented in the Synge and Griffith book but thanks Weinstein for “his advice and criticism” (Kohn 1945). The second paper was completed and submitted in November 1944 at a time when Kohn was engaged in advanced basic training at Camp Borden, Ontario. This substantial piece of work (Kohn 1946) establishes bounds on the motion of a heavy spherical top using a contour integration method used by Weinstein (1942) to study a spherical pendulum. The text makes clear that Kohn had at least some familiarity with *Über die Theorie des Kreisels* (1898), the great treatise on tops by Felix Klein and Arnold Sommerfeld.

In the 1945–1946 academic year (WK98),

after my discharge from the army, I took an excellent crash masters program, including some senior courses I had missed, graduate courses, and a master’s thesis consisting of my paper on tops and a paper on scaling atomic wave functions.

The atomic wave functions paper, “Two Applications of the Variational Method to Quantum Mechanics” (Kohn 1947) was the first of many to come (including the density functional papers) where Kohn exploits a variational principle. He first learned about such principles from an advanced undergraduate course where Weinstein discussed the Lagrangian and Hamiltonian formulations of classical mechanics. Weinstein regarded Kohn as a potential Ph.D. student and thus shared with him his recent work on variational methods to study the vibrations of clamped plates and membranes (Aronszajn and Weinstein 1942). A review paper by Weinstein (1941) summarized the original contributions to this subject by Lord Rayleigh and Walter Ritz.

Notwithstanding the foregoing, it was Applied Mathematics Professor Arthur Stevenson who broadened Kohn’s perspective to include quantum problems and the use of variational methods to study them. He is thanked in Kohn (1947) “for his kind advice and interest”.<sup>26</sup> Stevenson’s early research concerned quantum mechanical methods to calculate the energy levels of electrons in atoms, and he had performed variational calculations for the helium atom in collaboration with a colleague in the

<sup>25</sup> See footnote 2.

<sup>26</sup> Arthur Francis Chesterfield Stevenson (1899–1968) accepted a position in the Mathematics Department of the University of Toronto immediately after earning his B.A. from Trinity College, Cambridge in 1922. He returned to Cambridge in 1928 where he worked under the supervision of Ralph Fowler on a problem in theoretical spectroscopy which eventually led to his Ph.D. He returned to Toronto where he published original research and lectured on atomic physics, quantum mechanics, electromagnetic theory, scattering theory, and the differential equations of mathematical physics. He spent the last dozen years of his academic career on the faculty of Wayne State University in Detroit, Michigan (Duff 1969).

Toronto Physics Department (Stevenson and Crawford 1938). Kohn surely read this paper because the helium atom figured into his work also.

Kohn assumed that the readers of his paper were familiar with the variational method to find approximate solutions to the Schrödinger equation. Indeed, most textbooks of quantum mechanics written between 1930 and 1945 devoted more than passing attention to this topic because Egil Hylleraas had used it in 1929 with spectacular success to calculate the ionization energy of the helium atom. This provided the first convincing evidence that quantum mechanics could achieve quantitative success for a system of more than one electron.

For future reference, I sketch here a simple form of the Rayleigh–Ritz variational method appropriate to an  $N$ -electron system with ground-state energy  $E_0$  and Hamiltonian operator  $H$ . If  $\mathbf{r} = (x, y, z)$ , the starting point is a trial wave function,  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ , which depends on the Cartesian coordinates of all the electrons. One then computes a  $3N$ -dimensional integral with the configuration space volume element  $d\tau = d\mathbf{r}_1 \dots d\mathbf{r}_N$  and exploits the inequality,<sup>27</sup>

$$0 \leq E[\psi] = \int d\tau \psi^*(H - E_0)\psi = \int d\tau \psi^* H \psi - E_0. \quad (1)$$

The exact ground-state wave function  $\psi_0$  satisfies the Schrödinger equation,  $H\psi_0 = E_0\psi_0$ . Using the latter in Eq. (1) shows that  $E[\psi] = 0$  when  $\psi = \psi_0$  and suggests a strategy to find an upper bound to  $E_0$ : write the trial function  $\psi$  as a linear combination of a set of basis functions and minimize the integral on the right side of Eq. (1) with respect to the expansion coefficients. Increasing the number of basis functions generally lowers the bound obtained for  $E_0$ . An important feature of this procedure emerges if we consider a trial function of the form  $\psi = \psi_0 + \delta\psi$  where  $\delta\psi$  is “small” by some measure. Inserting this trial function into Eq. (1) gives the variation  $\delta E = E[\psi_0 + \delta\psi]$  as

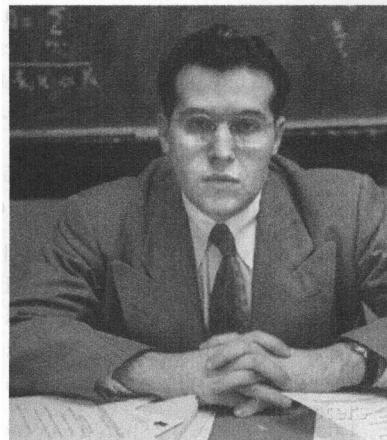
$$\delta E = \int d\tau (\psi_0 + \delta\psi)^* (H - E_0) (\psi_0 + \delta\psi) = \int d\tau \delta\psi^* (H - E_0) \delta\psi = O(\delta\psi^2). \quad (2)$$

One says that the energy functional  $E[\psi]$  is “stationary” in the sense that a trial function that differs from  $\psi_0$  by a small amount (first order in  $\delta\psi$ ) produces an energy which differs from  $E_0$  by an amount that is *very* small (second order in  $\delta\psi$ ). For that reason, minimizing  $E[\psi]$  with respect to a set of variational parameters produces a much better estimate for the ground-state energy than one might have supposed. The elegance and generality of this technique must have appealed powerfully to the young Kohn, because he “read many of the old papers on the subject and variational methods became the first tool in my theoretical physics toolbox” (WK12).

In the spring of 1946, Kohn completed his M.S. studies, taught calculus and analytic geometry as an Instructor for the Mathematics Department, and applied to a dozen or so Ph.D. programs with the clear idea to study theoretical physics. Offers of admission with financial support came from Rudolf Peierls at Birmingham and Eugene Wigner at

<sup>27</sup> It is necessary here that trial function satisfies  $\int d\tau \psi^* \psi = 1$  and that the integral  $\int d\tau \psi^* H \psi$  converges.

**Fig. 5** Julian Schwinger (ca. late 1940s) was Kohn's Ph.D. supervisor at Harvard University. Source unknown



Princeton, among others. Kohn accepted the Birmingham offer on the advice of Infeld, who knew Peierls personally (WK13b). One day later, an offer arrived from Harvard which included a prestigious Arthur Lehman Fellowship. Kohn again consulted Infeld, who without hesitation told him to communicate his regrets to Peierls, accept the offer from Harvard, and try to work for Julian Schwinger (Fig. 5).<sup>28</sup>

Accordingly, a somewhat insecure 23-year-old Walter Kohn arrived on the Harvard campus in the fall of 1946 as one of a group of about thirty first-year graduate students. The 28-year-old Schwinger had joined the Harvard faculty the previous spring and immediately began teaching a three-semester sequence of courses on special topics in theoretical physics (Schweber 1994). Kohn and his cohort stepped into the middle of this sequence as a supplement to their required courses in classical mechanics, electrodynamics, quantum mechanics, and statistical mechanics. In principle, Schwinger's course was devoted to nuclear physics. In practice, he devoted part of the time to a highly personal exposition of quantum mechanics in the style of Dirac (1935) and the rest of the time was given over to (PA99)

essentially everything Schwinger knew about. All about Green functions, all about nuclear physics and so on. All the numerical tricks he had devised to solve quantum mechanical problems and nuclear physics problems...there was a lot of physics and there were a lot of variational techniques, for example to solve the deuteron...He was also starting to build the machinery that was going to solve the problems of quantum electrodynamics. We were treated to a lot of that machinery.

Kohn himself has given one of the best descriptions of Schwinger's teaching style (Kohn 1996):

<sup>28</sup> Julian Seymour Schwinger (1918–1994) published ten papers in quantum mechanics and nuclear physics before the age of 21. He spent the war years working on waveguides for radar applications before turning his attention to quantum electrodynamics. The latter work earned him a one-third share of the 1965 Nobel Prize in physics (Martin and Glashow 1995; Mehra and Milton 2000).

Attending one of his formal lectures was comparable to hearing a new major concert by a very great composer, flawlessly performed by the composer himself...Old and new material were treated from fresh points of view and organized in magnificent overall structures. The delivery was magisterial, even, carefully worded, irresistible like a mighty river. He commanded the attention of his audience entirely from the content and form of his material, and by his personal mastery of it, without a touch of dramatization.

Quite early on, the chairman of the Harvard Physics Department, John Van Vleck, approached Kohn and asked him whether he would like to work with him on a solid-state physics problem.<sup>29</sup> Kohn was not interested in solid-state physics and instead presented himself to Schwinger as Infeld had urged him to do.<sup>30</sup> He described to Schwinger his experiences in Toronto (WK98, WK12)

Luckily for me, we shared a common interest in the variational methods of theoretical physics...He accepted me within minutes as one of his 10 PhD students. He suggested I should try to develop a Green function variational principle for three-body scattering problems, like low-energy neutron-deuteron scattering, while warning me ominously that he himself had tried and failed.

Schwinger was an acknowledged expert in the use of both variational principles and Green functions to solve a wide variety of problems. In Eq. (1), an energy functional  $E[\psi]$  with the stationary property  $\delta E = 0$  made it possible to estimate the ground-state energy of a bound-electron system such as helium. For a scattering problem, the energy is known and one is led to seek stationary variational functionals for other quantities. An example is the Green function, an energy-dependent operator defined in terms of the system Hamiltonian by

$$G(E) = \frac{1}{E - H}. \quad (3)$$

For two-body scattering, one writes  $H = H_f + V(\mathbf{r})$  where  $H_f\varphi = E_f\varphi$  is the Schrödinger equation for a free particle, and  $V(\mathbf{r})$  is the potential responsible for the scattering. Using a coordinate space representation of the corresponding free-particle Green function  $G_f$ , the scattered wave function  $\psi$  satisfies the integral equation,<sup>31</sup>

$$\psi(\mathbf{r}) = \varphi(\mathbf{r}) + \int d\mathbf{r}' G_f(\mathbf{r}, \mathbf{r}' | E_f) V(\mathbf{r}') \psi(\mathbf{r}'). \quad (4)$$

<sup>29</sup> John Hasbrouk Van Vleck (1899–1980) contributed widely to the fields of chemical physics, quantum electronics, and solid-state physics over a 46 years career at Harvard. In 1977, he was awarded a one-third share of the Nobel Prize in physics for his work in magnetism (Anderson 1987).

<sup>30</sup> Kohn had learned from his fellow graduate students about Wolfgang Pauli's famously negative view that solid-state physics was insufficiently fundamental and too approximate to attract the attention of a serious young theoretical physicist (von Meyenn 1989).

<sup>31</sup> It is necessary to replace  $E_f$  by the complex number  $E_f + i\epsilon$  in Eq. (3) and let  $\epsilon \rightarrow 0$  at the end to ensure that  $\psi$  behaves like an outgoing spherical wave (Baym 1969).

Kohn worked on the three-body Green function problem for half a year before abandoning it.<sup>32</sup> Instead, he generalized Eq. (1) and developed a variational principle for the two-body scattering phase shift, a quantity which characterizes the final state when two particles interact via a short-range potential.<sup>33</sup> He also derived a variational principle for the scattering amplitude for two-particle scattering with an arbitrary interaction potential. For both cases, Kohn borrowed from the Rayleigh–Ritz method and expanded the trial scattering wave function in a set of basis functions with the correct long-distance behavior. Finally, he derived a variational principle for the elements of the scattering matrix for the special case of nuclear collisions where multiple disintegrations are energetically forbidden. It is interesting that Kohn made no use of Schwinger's "beloved Green functions" (WK98) in his thesis, "Collisions of light nuclei," or in the published version of his thesis (Kohn 1948). He did, however, use his scattering amplitude variational principle to *rederive* an alternative variational principle for the phase shift that Schwinger had derived in his spring 1947 theoretical physics class using Eq. (3) and reported at a meeting of the American Physical Society (Schwinger 1947). The latter is commonly called "Schwinger's variational principle for scattering" (Adhikari 1998; Nesbet 2003).

Kohn did not have a close personal relationship with his advisor. None of Schwinger's students did, in part because it was notoriously difficult to schedule a personal meeting with him. Kohn met with him only "a few times a year" (Kohn 1996), and according to John David Jackson, an MIT graduate student who listened to Schwinger's lectures at Harvard, there was one occasion where "Kohn was miffed by Julian's unavailability. He completed his thesis, wrote up a paper, and submitted it to *Physical Review* without ever consulting him" (Mehra and Milton 2000). Such feelings must have passed quickly because, in a moving tribute at a memorial symposium after Schwinger's death, Kohn makes it clear that (Kohn 1996)

It was during these meetings, sometimes more than 2 hours long, that I learned the most from him...to dig for the essential; to pay attention to the experimental facts; to try to say something precise and operationally meaningful, even if one cannot calculate everything *a priori*; not to be satisfied until one has embedded his ideas in a coherent, logical, and esthetically satisfying structure...I cannot even imagine my subsequent scientific life without Julian's example and teaching.

Besides Schwinger, Kohn benefitted from members of his graduate student cohort who either contributed materially to his education at Harvard or who played an important role subsequently. One group consisted of fellow Schwinger students: Kenneth Case, Frederic de Hoffmann, Roy Glauber, Julian Eisenstein, Ben Mottelson, and Fritz Rohrlich. Another group did their Ph.D. work in other areas of physics: the theorists Thomas Kuhn, Rolf Landauer, and Philip Anderson, and the experimentalists

<sup>32</sup> This difficult and subtle problem was solved in the early 1960s by the Russian mathematical physicist Ludvig Faddeev (Faddeev 1965).

<sup>33</sup> At some point before he wrote up his thesis, Kohn learned that the Swedish physicist Lamek Hulthén had independently derived a variational principle for the scattering phase shift very similar to his own. Hulthén (1946) and Kohn (1948) begin with the same variational functional but propose slightly different variational procedures. The Kohn–Hulthén variational principle later found wide application in atomic, molecular, and nuclear scattering problems (Adhikari 1998; Nesbet 2003).

Nicolaas Bloembergen, George Pake, and Charles Slichter. Joaquin Luttinger, another MIT graduate student who made the short trip to Harvard to audit Schwinger's classes, later became a close friend and a scientific collaborator. All these members of Kohn's student network went on to have successful scientific careers.<sup>34</sup> Glauber, Mottelson, Anderson, and Bloembergen won Nobel Prizes themselves.

Walter's life changed profoundly in two important ways when he accepted an offer by Schwinger to remain at Harvard as a postdoctoral fellow. First, the income from this job permitted him to bring to Boston and marry Lois Mary Adams, a former nursing student he had met at the University of Toronto who had been working in New York City while he finished his Ph.D. (SDUT 2010). A baby daughter soon arrived, and family responsibilities were added to the research and teaching responsibilities that came with his position as Schwinger's assistant. The research project he undertook was an investigation of the electromagnetic properties of mesons done in collaboration with fellow Schwinger postdoc Sidney Borowitz. His teaching consisted of an introductory physics course in the summers of 1949–1950 and a junior/senior level classical mechanics course in the summer of 1950.<sup>35</sup>

The second profound change in Kohn's life occurred through the good offices of John Van Vleck, the solid-state theorist he had rebuffed as a thesis supervisor (Fig. 6). Van Vleck re-enters the story because Kohn supplemented his summer 1949 income by working for the Polaroid Corporation at their Cambridge, Massachusetts Research Laboratory. His job was to discover the mechanism whereby high-energy charged particles produce an image when they impinge on photographic plates.<sup>36</sup> This task required a knowledge of solid-state physics, which he acquired by reading Frederick Seitz' *The Modern Theory of Solids* (1940) and consulting with Van Vleck when necessary.

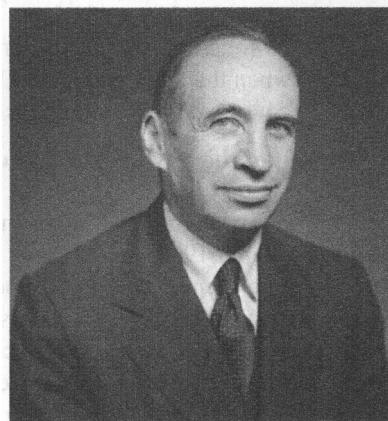
By this time, Kohn's first paper with Borowitz had appeared (Borowitz and Kohn 1949) and he had applied to the National Research Council for a fellowship to spend the 1950–1951 academic year with Wolfgang Pauli at the Eidgenössische Technische Hochschule in Zürich. Nevertheless, he was painfully aware that he had so far made only a "very minor contribution" to field theory research. This fact, and the stunning

<sup>34</sup> Josef Eisinger remained a close friend. He did his graduate work at MIT, just two miles down the Charles river from Harvard, and earned his Ph.D. in physics in 1951 for an experimental determination of the magnetic moment of K<sup>40</sup>. He spent 30 years at Bell Laboratories where he made a transition from solid-state physics to biophysics. From 1985 until his retirement in 1998, he taught and conducted research at the Mount Sinai School of Medicine in New York City (JE13).

<sup>35</sup> An evaluation of Kohn written by Ms. Norine T. Casey provides insight into Kohn's teaching style and philosophy of physics. Ms. Casey was a 1949 Wellesley graduate pursuing an MA in teaching at Harvard. As part of her curriculum, she attended Kohn's summer 1950 class (devoted to introductory optics, electricity, magnetism, atomic physics, and nuclear physics) and wrote a four-page evaluation of her experience. Kohn received a copy of her report (WKP. 1950. A critical analysis of Physics S-1b), which states that "Dr. Kohn's lectures were clear and concise. Demonstrations accompanied every lecture and were given with great enthusiasm... It was obvious from the beginning that [Dr. Kohn's] interest was not his own mastery of the mathematics, but in our understanding of the physics... It was not infrequent that he read from source material giving direct quotes [such] as Newton's relating his discovery of the diffraction of light".

<sup>36</sup> This technique had recently been introduced to study cosmic rays using plates produced by another company and Polaroid wanted to enter the business (Powell and Occhialini 1947).

**Fig. 6** Harvard's John Van Vleck facilitated Kohn's transition from nuclear physics to solid-state physics. Courtesy of the UW-Madison Archives



quality of the latest achievements by Schwinger and Richard Feynman, made him receptive when (WK98)

Van Vleck explained to me that he was about to take a leave of absence and “since you are familiar with solid-state physics,” he asked me if I could teach a graduate course on this subject he had planned to offer [for the fall 1949 semester]. This time, frustrated with my work on quantum field theory, I agreed.

Kohn not only taught the solid-state physics course, he collaborated with Harvard graduate student Richard Allan Silverman to find approximate numerical solutions of the Schrödinger equation for the purpose of calculating the cohesive energy of metallic lithium (Silverman and Kohn 1950).<sup>37</sup> Using the same numerical data, he and Bloembergen estimated the Knight shift for lithium, the latter being a measure of the electron wave function amplitude at the atomic nucleus accessible to experimenters using magnetic resonance techniques (Kohn and Bloembergen 1950). It is notable that Silverman and Kohn conclude with the remark, “One of us (W. Kohn) is investigating the cohesive energy by means of a variation iteration procedure based on the integral equation [Eq. (4) of this paper] and a Green function appropriate to a periodic lattice”.

Kohn, a naturalized Canadian citizen since 1943, looked everywhere in Canada and the United States for an entry-level academic position. Nothing turned up, but an early 1950 interview trip to the Westinghouse Research Laboratory in Pittsburgh, Pennsylvania, bore fruit even though his foreign citizenship precluded a job offer from Westinghouse. In Pittsburgh, Kohn stayed at the home of Alfred Schild, a friend from Toronto who had found a job teaching mathematics at the Carnegie Institute of Technology. Schild told him that the chairman of the Physics Department, Frederick Seitz, had just resigned and was moving his solid-state group to the University of Illinois (Seitz 1994). Perhaps, there was an opportunity at Carnegie Tech itself. The new chair, nuclear physicist Edward Creutz, interviewed Kohn and offered him a job

<sup>37</sup> Silverman's Ph.D. thesis states that “The author wishes to express his indebtedness to Professor Walter Kohn for suggesting the problem and for invaluable guidance during a large portion of the work (RS51). A generation of English-speaking solid-state physicists have Silverman to thank for his translation into English of *Methods of Quantum Field Theory in Statistical Physics* by Abrikosov et al. (1963).

as an Assistant Professor 48 h later.<sup>38</sup> It turned out that Creutz needed someone who could teach solid-state physics and mentor a few graduate students who had lost their advisors when the Seitz group left (WK98). Kohn was delighted to accept.

### 3 Portrait of the physicist as a Young Man

Walter Kohn was thinking about the start of his academic career at Carnegie Tech when, in March 1950, the National Research Council approved his application for a fellowship to spend a year in Europe. Ed Creutz agreed to a 1-year leave of absence, but only if Walter agreed to teach solid-state physics for the fall 1950 semester. At the same time, Kohn was having second thoughts about his original plan to work with Wolfgang Pauli. This led him to seek and secure the approvals needed to switch the venue for his fellowship year from Zürich to Niels Bohr's Institute for Theoretical Physics in Copenhagen. Accordingly, Kohn moved to Pittsburgh, taught his course, and left for Copenhagen at the end of the term.<sup>39</sup> When he arrived at the Institute in January 1951, Walter Kohn was an expert in scattering theory who had begun to think of himself as a solid-state physicist. Unfortunately, 'no one in Copenhagen, including Niels Bohr, had even heard the expression "solid-state physics"' (WK98).

Kohn managed to publish two papers that year, but more important to his future was the fact that the Institute attracted a steady stream of short-term and long-term visitors from around the world from whom he could learn new physics.<sup>40</sup> It was good luck for Kohn that postwar freedom of movement motivated Bohr to organize a meeting for all foreign physicists who had ever worked at the Institute (Rozental 1967). The resulting Conference on Problems in Quantum Physics (July 6–10 1951) was attended by an outstanding collection of theoretical physicists, many of whom Walter was able to incorporate into his expanding professional network.<sup>41</sup> A few weeks later, Kohn

<sup>38</sup> Edward Chester Creutz (1913–2009) earned his Ph.D. in experimental nuclear physics from the University of Wisconsin in 1938. He moved to Princeton as an Instructor and used their cyclotron for nuclear physics projects until the Manhattan Project redirected his efforts to the synthesis of plutonium and the triggering of the plutonium bomb. After the war, Creutz joined the faculty at Carnegie Tech to direct the construction of a proton synchrocyclotron and to build an experimental nuclear physics group. After 9 years (seven as chair), Creutz moved to San Diego, California, to help found the General Atomics Division of General Dynamics Corporation. He spent 15 years there before concluding his career as Associate Director of the National Science Foundation (Hinman and Rose 2010).

<sup>39</sup> One former Carnegie Tech graduate student remembers Kohn's solid-state physics lectures as well-prepared, clearly delivered, and mathematically precise. He was surprised when the final exam avoided mathematical issues and focused entirely on qualitative aspects of the subject (AA13).

<sup>40</sup> Aage Bohr and Christian Møller were already fixtures at the institute. Kohn's Harvard classmate Ben Mottelson arrived in the fall of 1950 and never left. A partial list of visitors who overlapped with Kohn for at least some time includes Hendrik Casimir, Freeman Dyson, Ugo Fano, Nicolas Kemmer, Louis Michel, Wladyslaw Swiatecki, Jean Valatin, Nicolaas van Kampen, and Arthur Wightman. NBA 1951 Guest Book of the Institute for Theoretical Physics.

<sup>41</sup> A partial list of attendees includes Hans Bethe, Homi Bhabha, Léon Brillouin, Richard Dalitz, Paul Dirac, Maria Mayer, Dirk ter Haar, Werner Heisenberg, Walter Heitler, Léon van Hove, Lamek Hulthén, Egil Hylleraas, Hendrik Kramers, Ralph Kronig, Jens Lindhard, Lise Meitner, Wolfgang Pauli, Rudolf Peierls, Léon Rosenfeld, John Slater, Ernst Stueckelberg, Victor Weisskopf, Gregor Wentzel, John Wheeler, and Gian-Carlo Wick. NBA. Program and Participants for the Conference on Problems in Quantum Physics. July 6–10, 1951. Institute for Theoretical Physics.

was tapped to lecture on solid-state physics for 2 weeks at the first Summer School of Theoretical Physics organized by Cécile DeWitt at Les Houches, near Chamonix in the French Alps.<sup>42</sup>

At the end of 1951, Bohr wrote a formal evaluation which concluded that<sup>43</sup>

Dr. Kohn has proved himself a highly qualified theoretical physicist with great knowledge of a wide field of problems. His ability to stimulate others in their work and his willingness to assist them with his knowledge has been of great value to the many members of our group.

This good opinion led Bohr to arrange a Rask Ørsted Foundation fellowship for Kohn so he could remain in Copenhagen through the summer of 1952. This was welcome news because Walter and his family enjoyed living in Denmark. Moreover, he had just begun a scientific collaboration with Res Jost, a Swiss mathematical physicist 5 years his senior who had lectured on quantum field theory at the Les Houches Summer School.<sup>44</sup> Jost was interested in scattering theory, and his “predilection for mathematical rigor” (Enz 2002) struck a responsive chord in Kohn. Together, the two theorists completed three papers (including an “inverse scattering problem” where one deduces characteristics of the scattering potential from phase shift information) before Kohn returned to Carnegie Tech to begin the 1952–1953 academic year (Jost and Kohn 1952a,b, 1953). On his own, Kohn studied the validity of the Born expansion for scattering (Kohn 1952a) and a non-Green function variational principle for electron waves in a periodic potential (Kohn 1952b).

Back in Pittsburgh, the Physics Department had changed somewhat during Walter’s absence. The senior experimentalist Immanuel Estermann had left to head the physics section of the Office of Naval Research (ONR), and his last Ph.D. student, Simeon Friedberg, had taken over his low-temperature physics laboratory. A senior theorist, Gian-Carlo Wick, had joined the faculty from Berkeley, and Roman Smoluchowski, an expert in the theory of defects in solids, had transferred to the Physics Department from the Metallurgy Department. A young experimenter, Jacob Goldman, and a young theorist, Paul Marcus, had joined the solid-state physics group to complement the senior experimentalist Emerson Pugh. One familiar face was Norman Rostoker, a Toronto native who had graduated from his hometown university as a physics major 1 year behind Kohn and then received his Ph.D. at Carnegie Tech under Pugh’s supervision (Rostoker 2003, NR13). Kohn and Rostoker had become friends during the fall 1950 semester, and Norman was still working in the Physics Department as a postgraduate research scientist when Kohn returned from Europe.

The fall 1952 semester found Kohn teaching thermodynamics to undergraduates and nuclear physics to graduate students. He was also named as co-principal investigator

<sup>42</sup> Kohn was an emergency replacement for Mario Verde, a nuclear physicist who had fallen ill (DeWitt 1951, CDW13).

<sup>43</sup> NBA. Evaluation of Walter Kohn 1951.

<sup>44</sup> Res Jost (1918–1990) wrote his Ph.D. thesis under the supervision of Gregor Wentzel and spent 3 years as the principal assistant to Wolfgang Pauli. He was a senior fellow at the Institute for Advanced Study in Princeton for 6 years (1949–1955) before accepting a professorship at the Eidgenössische Technische Hochschule in Zürich. Jost’s research focused on mathematical physics and quantum field theory, particularly axiomatic versions of the latter. (Kohn et al. 1992; Pais 1996).

with Jack Goldman on an ONR contract to conduct solid-state research.<sup>45</sup> His main research project was to develop a Green function method to calculate the energy band structure for crystalline solids. In other words, he wanted to use Eq. (3) to solve the Schrödinger equation to find the energy eigenfunctions and eigenvalues for electrons moving in a periodic potential. A distraction arose in the spring 1953 semester when Carnegie Tech learned that Walter had received job offers from the Department of Mathematics at McGill University in Montreal and the Physical Research Department at Bell Telephone Laboratories in Murray Hill, New Jersey. Evidently, others besides Niels Bohr had formed a very positive impression of this new Assistant Professor. In the end, Carnegie Tech retained his services by promoting him to Associate Professor after only three semesters of academic service.<sup>46</sup>

Kohn had brought to Carnegie Tech the germ of his Green function method to solve the electron band-structure problem. He recruited Norman Rostoker to help with the numerical calculations and that activity continued (part time) while Walter was in Copenhagen.<sup>47</sup> The work accelerated when Kohn returned to Pittsburgh and he reported their still unpublished results at two invited talks, one at the June 1953 Summer Meeting of the American Physical Society and one at the July 1953 Gordon Research Conference devoted to the Physics and Chemistry of Metals. The latter was a particularly prestigious venue, and it is notable that of the seven theorists invited to speak, the three youngest (by far) were Walter Kohn, Jacques Friedel, and David Pines.<sup>48</sup> Friedel, an expert on the theory of metals and alloys, and Pines, an expert on electron-electron interactions in solids, had both published half a dozen papers in their fields by the time of the Gordon Conference. It is an indication of Kohn's rising reputation that he had published only one full-length paper in solid-state physics by this time. Kohn's Green function paper (Kohn and Rostoker 1954) finally appeared in the June 1, 1954, issue of the journal *Physical Review*. Therein, he and Rostoker (WK98)

developed a theory for the energy band structure of electrons in solids harking back to my earlier experience with scattering, Green functions, and variational methods. We showed how to determine the band structure from a knowledge of purely geometric structure constants and a small number ( $\sim 3$ ) of scattering phase shifts of the potential in a single sphericalized cell.

It happens that the same basic idea had been published several years earlier by the Dutch physicist Jan Korringa. However, Korringa (1947) included no numerical applications

<sup>45</sup> For 15 years after World War II ended, most solid-state physics research in the United States was funded by the Office of Naval Research. Most nuclear physics research was supported by the United States Atomic Energy Commission (Old 1961; Sapolsky 1990).

<sup>46</sup> WKP. January 12, 1953, letter to Walter Kohn from R.A. Deller, Bell Telephone Laboratory; February 13 letter to Walter Kohn from H. Tate, McGill University; February 24 letter to Walter Kohn from Edward Creutz, Carnegie Institute of Technology.

<sup>47</sup> The actual computing was performed by a "computress" named Alice Watson who operated a Friden Model STW-1 Electro-Mechanical Calculator. Although her equipment changed to an IBM 650 digital computer in 1956, she continued to do computing tasks for Kohn the entire time he worked at Carnegie Tech (AY13).

<sup>48</sup> WKP. Final program of the July 1953 Gordon Research Conference on the Physics and Chemistry of Metals.

and his paper went largely unnoticed.<sup>49</sup> Kohn and Rostoker illustrated their method by calculating the energy as a function of wave number for the 2s conduction band of lithium metal and comparing their results with previous calculations in the literature. It is entirely characteristic of Kohn that he did *not* take his band-structure formalism and begin applying it to one material after another.<sup>50</sup> Instead, he made one use of his lithium results (Kohn 1954) and then proceeded to expand his personal research activities into other areas of solid-state physics. To understand the choices he made, we interrupt our narrative briefly to survey the research agenda of solid-state physics in the mid-1950s.

Wartime developments in computers, instrumentation, and materials processing had a profound effect on the issues addressed by solid-state physicists at the mid-point of the twentieth century.<sup>51</sup> In June 1954, the National Science Foundation and the American Society for Engineering Education sponsored a meeting at Carnegie Tech attended by representatives from 45 colleges and universities and several industrial and government laboratories. According to the conference co-chair, Professor Jack Goldman,<sup>52</sup> the purpose of the meeting was to "make more definitive the state of knowledge of solid-state physics and the levels at which various parts of it may be expected to be integrated into engineering education" (Goldman 1957). To this end, the conferees identified six broad areas of active solid-state physics research: the structure of crystalline matter, metals and alloys, surfaces, magnetism, semiconductors and dielectrics, and non-crystalline materials.

One needed to attend conferences reserved for specialists to learn the cutting edge issues in each area. Happily, the same purpose was soon served by the articles published in *Solid-State Physics*, a series of volumes initiated by Frederick Seitz and David Turnbull in 1954 to provide "broad surveys of fields of advanced research that serve to inform and stimulate the more experienced investigator" (Seitz and Turnbull 1955). The inaugural volume contained articles devoted to five issues: the band-structure problem, the properties of valence semiconductors, electron-electron interactions, cohesion in solids, and the theory of order-disorder phase transitions. Kohn had already made a significant contribution to band-structure theory, and he now added to his repertoire research projects devoted to semiconductors and to the effects of the electron-electron interaction (soon relabeled many-body physics). The total energy

<sup>49</sup> Korringa (1994) relates that "computers were rare in the Netherlands in 1946 and a cost estimate [for a numerical application] exceeded the annual research budget of our theory group".

<sup>50</sup> Kohn left the development and application of the Korringa-Kohn-Rostoker (KKR) method to others. It eventually became a standard method of band-structure calculation (Zabludil et al. 2005).

<sup>51</sup> Hoddeson et al. (1992) is a history of solid-state physics up to about 1960. The autobiography of Seitz (1994) provides a broad view from the perspective of a major player in the development of solid-state physics as the discipline matured through the 1950s and 1960s.

<sup>52</sup> Jacob E. Goldman (1921–2011) was born in Brooklyn, New York and studied physics at Yeshiva University and the University of Pennsylvania. His expertise in magnetism led him to the Westinghouse Research Laboratory in 1945 before he joined the faculty of the Carnegie Institute of Technology in 1951. He moved to the nascent Scientific Research Laboratory of the Ford Motor Company in 1955 and eventually became head of all Ford's corporate research and development. He joined the Xerox corporation in 1969 and 1 year later founded their Palo Alto Research Center (PARC). The first modern personal computer and the first graphical user interface were invented at PARC a few years later (Markoff 2011).

**Fig. 7** Joaquin Luttinger was Kohn's principal scientific collaborator in the 1950s.  
Courtesy of Walter Kohn



(cohesion) problem became a central concern when he developed density functional theory a decade later.<sup>53</sup>

Kohn became interested in semiconductors because his flirtation with permanent employment at Bell Telephone Laboratories led to a summer consulting arrangement that lasted from 1953 to 1966. His first summer project, a theoretical study of the damage done to germanium crystals after bombardment by energetic electrons, was motivated by experimental results obtained at Bell Labs by Walter Brown and Robert Fletcher (Brown et al. 1953). These experiments, in turn, were part of an enormous in-house effort to investigate the properties of the elemental semiconductors germanium and silicon after the 1947 invention of the transistor at Bell Labs by John Bardeen, Walter Brattain, and William Shockley (Millman 1983). Kohn was happy to return to Bell Labs Summer after summer, both to gain access to exciting experimental results and for the opportunity to interact with senior theorists on the Bell Labs staff like Conyers Herring and Gregory Wannier and junior theorists closer to him in age like Peter Wolff and his Harvard classmate Philip Anderson. He would later remark that "I owe this institution my growing up from amateur to professional" (WK98).

Walter's 1954 "summer vacation" at Bell Labs was particularly important because he began a long-lasting scientific collaboration with Joaquin Luttinger (Fig. 7), another

<sup>53</sup> Kohn never worked personally in the field of thermal phase transitions. Nevertheless, he often supported a postdoctoral fellow trained in statistical mechanics to work on this class of problems. See Domb (1996) for a history of this subject.

consultant to the semiconductor group.<sup>54</sup> They worked together to create a rigorous “effective mass theory” for the electronic energy levels produced when impurity atoms are purposely substituted for germanium or silicon atoms in pure crystals of the latter. The crucial importance of these impurities and their quantum mechanical states to the extraordinary electrical properties of semiconductors had been explained qualitatively by William Shockley in his seminal treatise, *Electrons and Holes in Semiconductors* (1950). However, careful electron spin resonance and cyclotron resonance experiments at Bell Labs and elsewhere demanded a quantitative theory. Not for the first time and not for the last time, Kohn combined the creation of a novel and sophisticated theory with variational calculations designed to produce numbers for comparison with measurements for specific material systems. That fall, Kohn and Luttinger completed three substantial papers in semiconductor physics (Luttinger and Kohn 1955; Kohn and Luttinger 1955a,b) and thereby finished in a virtual dead heat with Berkeley solid-state theorist, Charles Kittel, who published similar work independently (Kittel and Mitchell 1954; Dresselhaus et al. 1955).<sup>55</sup>

In the spring of 1955, Walter worked hard to convince the British theoretical solid-state physicist Harry Jones to accept an offer of a chaired position at Carnegie Tech. Jones had co-authored (with Nevill Mott) the influential book *The Theory of the Properties of Metals and Alloys* (1936), and he had spent the spring 1954 semester as a visiting professor in Kohn’s department. Kohn wrote to Jones and pointed out that “all of us in solid-state physics, as well as all the people in metallurgy, would be delighted to see you come here. With your field of interest, I honestly think that probably no other school in this country could offer you better opportunities for creative work along research and teaching lines”.<sup>56</sup> Jones ultimately declined for personal reasons. The undeterred Kohn pursued the physics of semiconductors and metals simultaneously and submitted two manuscripts to the *Physical Review*. The first paper, co-authored with his first Carnegie Tech Ph.D. student, Daniel Schechter, reported calculations for the wave functions and energy levels associated with shallow (weakly bound) impurity states in germanium.<sup>57</sup> The second paper reported a Knight shift calculation for metallic sodium with Terje Kjeldaas, a full-time employee of the Westinghouse Research

<sup>54</sup> Joaquin Mazdak Luttinger (1923–1997) earned his B.S. in physics at the Massachusetts Institute of Technology and remained there to complete a Ph.D. thesis (1947) in statistical physics under the supervision of Laszlo Tisza. He worked on quantum electrodynamics as the first American postdoctoral fellow of Wolfgang Pauli but reverted to problems in many-body theory, solid-state physics, and statistical mechanics for the rest of his career as a professor, primarily at Columbia University (1960–1993) (Anderson et al. 1997).

<sup>55</sup> The Bell Laboratories experimenter Robert Fletcher recalled that “Walter was a very kind and thoughtful person to work with. I never had the impression he looked down on us experimenters as some theorists are inclined to do” (RF13). Another Bell Laboratories experimenter who published papers related to the Kohn-Luttinger theory was Walter’s old friend Josef Eisinger (Eisinger and Feher 1958).

<sup>56</sup> WKP. April 20, 1955, letter from Walter Kohn to Harry Jones.

<sup>57</sup> Another graduate student, James Montague, never quite finished a thesis devoted to deep (strongly bound) impurity levels in semiconductors (LG13).

Laboratories in East Pittsburgh (Kohn and Schechter 1955; Kjeldaas and Kohn 1956).<sup>58</sup>

For later reference, it is important to note that Kohn acted as an informal consultant to the transition-metal magnetism groups of his faculty colleagues Emerson Pugh and Jack Goldman. Goldman's Ph.D. student Anthony Arrott recalls Kohn's surprise when Arrott successfully used a simple energy band model to analyze his magnetic data for concentrated Cu–Ni alloys. At Arrott's oral thesis defense (AA13), Kohn asked him a question that foreshadowed his motivation to invent density functional theory 10 years later: "how can you use a band model when the potential felt by the electrons is not periodic?"

As 1955 turned into 1956, Walter found himself thinking more and more about the effective mass equation he had derived with Luttinger for the energy levels of impurity states in silicon. Their "one-particle" method treated the impurity atom as unaware of its silicon host except for whatever influence could be captured by two numbers: an effective mass  $m^*$  which parameterized the arrangement of atoms in the silicon crystal and an effective dielectric constant  $\kappa^*$  which parameterized the ability of the silicon conduction electrons to "screen" or "shield" the Coulomb potential produced by a positively charged impurity embedded in the semiconductor.<sup>59</sup> Why then did the energy levels calculated using the effective mass equation agree so very well with the energy levels measured in the laboratory? Surely, he reasoned, it must be that "this equation can be derived from some very general properties of the entire many-electron wave function without any recourse to the one-particle picture" (Kohn 1957b). For the first time, Kohn attacked the quantum-mechanical "many-body problem" in solid-state physics where the repulsive Coulomb interaction between all pairs of electrons is taken seriously. Working alone, he managed to demonstrate his assertion for a hypothetical situation where the charge on the impurity nucleus exceeds that of the other nuclei by an infinitesimal amount. He announced this result in a comprehensive review of the Kohn–Luttinger theory written for Seitz and Turnbull's *Solid-State Physics* series (Kohn 1957a). A full account appeared later (Kohn 1957b).

Meanwhile, back at Bell Labs, the resident theoretical physicists had successfully convinced the vice president for research, William Oliver Baker, to create (Anderson 2011)

a separate 'super-department' for theorists...with postdoctoral fellows, a rotating boss on whose identity we were consulted, sabbaticals, a travel budget under our

<sup>58</sup> Kjeldaas pursued his Ph.D. part time at the University of Pittsburgh. His 1959 thesis thanks Kohn and Westinghouse solid-state theorist Theodore Holstein for acting as co-supervisors (TK59). Westinghouse was a lively place for solid-state physics in the mid-1950s under the leadership of its Director of Science, Clarence Zener, himself a solid-state theorist. The theorists he recruited to complement Holstein included Edward Neufville Adams, Petros Argyres, William Mullins, and Yako Yafet. The experimenters hired by Zener included Raymond Bowers, Robert Keyes, Colman Goldberg, and John Rayne. Walter Kohn had a consulting arrangement with Westinghouse. Holstein, Adams, and Yafet occasionally taught classes at Carnegie Tech (AA13, VA13).

<sup>59</sup> By "screening" or "shielding," we mean that the electrons nearest to the positive charge are attracted to it and thereby partially neutralize the Coulomb force exerted by the positive charge on distant electrons and ions.

control, and a spectacular summer visitor program...One of the reasons for our success with management was the fact that for several years we had had Walter Kohn and Quin Luttinger as regular summer visitors and they had become so useful that our bosses desperately wanted to attract them permanently.

The advent of a “spectacular summer visitor program” meant that an unusually large number of theoretical physicists passed through and interacted with Kohn and Luttinger during their 1956 summer stay at the Labs.<sup>60</sup> A hot topic was the effect on the properties of semiconductors when one systematically increased the number of impurities present. When the impurity concentration is low and the temperature is low, it was well known that electron scattering from impurities is the main source of a solid’s electrical resistance. What happens when the concentration of impurities is high? Luttinger had been thinking about the general subject of electric current flow in solids already in connection with his studies of the Hall effect in ferromagnets, and it was not difficult to convince Kohn to work with him to produce as rigorous a theory of electrical conductivity as they could.<sup>61</sup> After all, Luttinger’s understanding of the experimental facts for the Hall effect came directly from a review paper written by Kohn’s Carnegie Tech colleagues Emerson Pugh and Norman Rostoker (Pugh and Rostoker 1953). The fruits of that summer’s labors were two long papers on the quantum theory of electrical transport in solids<sup>62</sup> (Kohn and Luttinger 1957; Luttinger and Kohn 1958). In contrast to their effective mass theory work, which more reflected Kohn’s style to address important physical questions with intuition, a good idea, and mathematical elegance, the transport theory papers more reflected Luttinger’s preference for general formalism and mathematical rigor. In this way, the two young theorists enlarged each others’ perspectives of their craft.

For Walter Kohn, professor of physics, the calendar change from 1956 to 1957 meant little more than a change in his teaching assignment from statistical mechanics for physics majors to classical physics for engineers. However, for Walter Kohn, solid-state physicist, the new year saw changes in his field that had a profound effect on his future research efforts. In the words of Canadian physicist Allan Griffin, 1957 was a “magic year” when “the way all theoretical physicists thought about interacting many-body systems underwent a revolution” (AG07). The key event was the realization that the methods of quantum field theory could be applied with equal success to study the

<sup>60</sup> Visitors to the theory group that summer included Elihu Abrahams, Kerson Huang, David Pines, J. Robert Schrieffer, and Philippe Nozières (Anderson 1978).

<sup>61</sup> The Hall effect refers to a voltage that appears across a current-carrying sample when a magnetic field is applied in a direction perpendicular to the direction of current flow (Chien and Westgate 1980).

<sup>62</sup> Kohn and Luttinger did not ultimately address the problem of the effect of a large concentration of impurities on the electrical conductivity of a semiconductor. This was done by Anderson (1958). Simultaneous with Kohn and Luttinger’s work on quantum transport, the Japanese physicist Ryogo Kubo proposed a theoretical approach to the same problem which ultimately became standard (Kubo 1957).

many-electron problem in solid-state physics.<sup>63</sup> In particular, diagrammatic methods like those invented by Feynman (1949) to study quantum electrodynamics made it possible to define a perturbation theory that remained consistent as the number of particles in a system increased. Feynman diagrams posed no problem for a Harvard Ph.D. like Kohn who was both well trained in quantum mechanics and familiar with quantum field theory from Julian Schwinger's lectures. He also had a ready-made problem: his own desire to understand the success of the Kohn–Luttinger effective mass equation from a many-body point of view. A breakthrough paper by Goldstone (1957) provided all the technical details he needed.

Walter became a naturalized citizen of the United States in 1957, and he had arranged a sabbatical leave from Carnegie Tech for the 1957–1958 academic year. He spent the fall of 1957 at the Physics Department of the University of Pennsylvania, and it was there that he wrote up Kohn (1958), his first contribution to the many-body revolution—a diagrammatic analysis of the static dielectric constant of an insulator. At the end of this paper, Kohn acknowledges “stimulating conversations” with Keith Brueckner, a senior member of Penn’s Physics Department whose own thinking about the quantum many-body problem had stimulated Goldstone’s work.<sup>64</sup> Brueckner, in turn, led an effort by his Penn colleagues to hire Kohn away from Carnegie Tech. A similar effort was mounted by the Physics Department of the University of Chicago.<sup>65</sup> Kohn took these overtures seriously, and Carnegie Tech responded by awarding him tenure and promoting him to the rank of Professor with a substantial increase in salary.<sup>66</sup> Walter made his decision to return to Pittsburgh while completing his sabbatical and spending the spring 1958 semester with Harry Jones and his group at the Department of Mathematics of the Imperial College of Science and Technology in London.

The many-body revolution introduced new ideas into solid-state physics like the quasi-particles of Landau (1956) and new objects for study like the one-particle and two-particle Green functions exploited by Galitskii and Migdal (1958).<sup>67</sup> The physical and mathematical elegance of this subject caused some solid-state theorists to

<sup>63</sup> There is no definitive history of this revolution. Different points of view can be found in Pines (1961), Chapter 8 of Hoddeson et al. (1992), Gell-Mann (1996), Brueckner (2000), and Kaiser (2005). Percus (1963) is the proceedings of a January 28–29, 1957, meeting convened at the Stevens Institute of Technology “for the purpose of bringing together workers in the numerous rapidly moving fields of many-particle physics”. The contributions to this volume (particularly the roundtable discussions) paint a vivid picture of the first months of the revolution. The Bardeen–Cooper–Schrieffer theory of superconductivity appeared later the same year, but Bardeen et al. (1957) makes no explicit use of field theoretic methods.

<sup>64</sup> Keith Allen Brueckner (1924–) studied mathematics at the University of Minnesota before earning his Ph.D. in physics (1950) from the University of California (Berkeley) under the supervision of Robert Serber. As a professor at Indiana University and the University of Pennsylvania in the 1950s, Brueckner made many significant contributions to the theories of nuclear matter and the electron gas. In 1959, he became the first member of the Physics Department at the newly created University of California, San Diego. Brueckner divided his professional activities between academia, industry, and the government until his retirement from UCSD in 1991.

<sup>65</sup> WKP. October 7, 1957, letter from Frederick Reif to Walter Kohn.

<sup>66</sup> WKP. January 29, 1958, letter from Carnegie Tech President J.C. Warner to Walter Kohn.

<sup>67</sup> The Green functions used in many-body theory are the ground-state expectation values (averages over the ground-state many-body wave function) of various quantum mechanical operators. The Green function for the Schrödinger partial differential equation, Eq. (2), is related to some of the Green functions used in many-body theory when all the forces between the particles are turned off.

focus their attention exclusively on problems where many-body effects dominate the physics.<sup>68</sup> Kohn did not follow this particular path because not every problem that interested him demanded a many-body analysis. For example, a theorem due to Bloch (1928) demonstrated that the eigenfunctions and energy eigenvalues of the Schrödinger band for a spatially periodic system like a crystal have the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u_{\mathbf{k}}(\mathbf{r}) \quad \text{and} \quad E(\mathbf{k}), \quad (5)$$

where the three quantum numbers collected in the vector  $\mathbf{k} = (k_x, k_y, k_z)$  are real numbers confined to a finite volume of the three-dimensional  $\mathbf{k}$ -space called the Brillouin zone, and the function  $u_{\mathbf{k}}(\mathbf{r})$  has the spatial periodicity of the crystal. While at Imperial College, Kohn performed an extensive study of the properties of the Bloch solutions when  $\mathbf{k}$  is a complex-valued vector. This allowed him to make precise statements about the exponential decay of a class of spatially localized wave functions first introduced by Wannier (1937). In a separate project, Kohn analyzed the motion of Bloch electrons in a magnetic field with more rigor than had been done previously. He succeeded to show that an approximation for this problem first made by Peierls (1933) had a much broader range of validity than previously thought.

Kohn's Imperial College projects in mathematical physics<sup>69</sup> did not disengage him from the more practical aspects of solid-state physics. For example, he was invited to the 1958 International Conference on Semiconductors in Rochester, New York, to report his many-body analysis of the effective mass equation for shallow impurity states. While there, he attended a session devoted to the calculation of energy bands and listened to a talk by fellow theorist James Phillips. Kohn asked Phillips whether he was doing "physics or magic" because Phillips' "pseudopotential method" reproduced the results of much more elaborate band-structure calculations for silicon and germanium using only three parameters for each (Bassani and Tosi 1988). Similarly, Kohn paid careful attention when the *phonon spectrum* of a crystal was measured for the first time (Brockhouse and Stewart 1958) and also when the *Fermi surface* of a metal was measured for the first time (Pippard 1957; Gold 1958).<sup>70</sup>

These experimental breakthroughs stimulated Walter's scientific imagination, and he soon completed a simple and elegant analysis which predicted that the phonon spectrum of a metal possesses observable "anomalies" which depend only on the existence and shape of the Fermi surface. More precisely, the Fermi surface locates a singularity in a linear response function which describes the ability of the conduction electrons to screen the ions which move during a lattice vibration. The short communication that described what came to be known as "Kohn anomalies" was one of four manuscripts he submitted for publication during the 1958–1959 academic year at Carnegie

<sup>68</sup> Samuel F. Edwards, another Schwinger Ph.D. student who switched from nuclear physics to solid-state physics, has remarked that "the Green function formalism is very good to write down solutions in abstract exact form, which gives unassailable answers when used in comparatively simple situations" (Edwards 1998).

<sup>69</sup> Kohn became an Associate Editor of the *Journal of Mathematical Physics* in 1961.

<sup>70</sup> A phonon is a quantized lattice vibration in a crystal. The Fermi surface is the constant energy surface in the Bloch  $\mathbf{k}$ -space for the most energetic electrons in a metal.

Tech (Kohn 1959a,b,c; Ambegaokar and Kohn 1959). Two longer papers described the results of the projects begun at Imperial College and the paper co-authored by his Ph.D. student Vinay Ambegaokar reported a new sum rule for insulators. The Kohn anomaly and Ambegaokar papers appeared in the same issue of *Physical Review Letters*, a journal spun off from the *Physical Review* to provide “speedy publication” of “new discoveries of major importance and for significant contributions to highly active and rapidly changing lines of research in basic physics” (PRL64).

Ambegaokar recalls that (Ambegaokar 2003, VA13)

Before going on leave [to Pennsylvania], Walter advised me to take a second course in quantum mechanics taught by Gian-Carlo Wick even though I had not finished a first course...Upon his return [from England], he suggested a research project that was very much to my taste. We met for at least an hour a week and his supervision was both precise and constructive. He thought hard during our meetings to keep the project moving along...[Walter] could be formal as a person, but he opened up considerably with people he respected. He got me a summer job at Bell Labs and we played tennis together there frequently.

Another student, James Langer, was an undergraduate physics major at Carnegie Tech from 1951 to 1955. Langer never took a formal course from Kohn, but in his senior year, “Walter somehow became my private instructor for a year-long supervised reading course. We went through the first edition of Leonard Schiff’s classic text *Quantum Mechanics* essentially cover to cover” (Langer 2003). Langer won a Marshall Scholarship to attend graduate school in Great Britain and Kohn directed him to Rudolf Peierls at the University of Birmingham.<sup>71</sup> Langer earned his Ph.D. for a problem in nuclear physics and then returned to Carnegie Tech as an Instructor in the fall of 1958. For the next year, he and Seymour Vosko (a recent Ph.D. student of Gian-Carlo Wick) functioned as postdoctoral fellows in Kohn’s theoretical solid-state physics group.

The problem Kohn set for Langer and Vosko was the shielding of a positively charged impurity embedded in a metal host. This is the analog of the problem Walter had studied previously for the case of a dielectric host. Kohn’s many-body perturbation theory calculation for the dielectric case confirmed the classical result that the Coulomb potential  $q/r$  at distance  $r$  from a point charge  $q$  in vacuum changes to  $q/\kappa r$  when the point charge is embedded in an insulator with dielectric constant  $\kappa$ . Mott (1936) studied the screening of a point charge in a metal in connection with a calculation of the electrical resistivity of dilute metal alloys. He used semi-classical Thomas–Fermi theory (March 1957) and showed that the potential  $q/r$  in vacuum changes to  $(q/r)\exp(-r/\ell)$  in a metal. The screening length  $\ell$  depends on the density of conduction electrons and takes the value 1–2 Å in a typical metal. Friedel (1958) revisited this problem using a scattering theory method and found that the disturbance of the electronic charge density at a distance  $r$  from the impurity charge,  $\delta n(r)$ , varied as

$$\delta n(r) \propto \frac{\cos(2k_F r + \Delta)}{r^3}, \quad (6)$$

<sup>71</sup> In this way, Langer became the Peierls Ph.D. student Kohn would have been if he had not gone to Harvard to work with Julian Schwinger (WK13b).

where  $k_F$  and  $\Delta$  are two constants. The  $1/r^3$  decay of this function falls off much more slowly with distance than the exponential variation predicted by Mott's theory and thus implies that the effect of isolated impurities might not be completely screened at the position of nearby atoms. The oscillatory behavior in Eq. (6) is an intrinsically quantum effect. Kohn did not fully believe Friedel's result and therefore asked his postdocs to attack the problem themselves (WK13b). Much to his surprise, Langer and Vosko (1959) fully confirmed Friedel's formula using diagrammatic many-body perturbation theory.<sup>72</sup> Kohn promptly asked Vosko to apply these results to a quantitative calculation of the magnitude of the nuclear magnetic resonance signal in copper metal when small amounts of impurity atoms are introduced (Kohn and Vosko 1960). Confirmation of the Kohn–Vosko theory came from comparison with experiments performed by Theodore Rowland at the Union Carbide Metals Company (Rowland 1960). Kohn knew Rowland from his Harvard days when Rowland was a Ph.D. student of Nicolaas Bloembergen.

The summer of 1959 reunited Walter and Quin Luttinger at Bell Laboratories. Once again, the pair produced an interesting paper (Kohn and Luttinger 1960), and once again, Kohn grappled with an offer from Keith Brueckner to leave Carnegie Tech. This time, however, Brueckner was not soliciting on behalf of the University of Pennsylvania. He had resigned from Penn a few months previously, and his mission now was to convince Walter to help him create the Physics Department at the soon-to-open University of California at La Jolla (later San Diego). Earlier in the year, Brueckner had flown Kohn to the beautiful site of the proposed campus to meet and hear the vision of its principal advocate, Roger Revelle, the Director of the Scripps Institute for Oceanography. The salary was attractive and La Jolla seemed like an ideal place to relocate his wife and two elementary school-aged daughters.<sup>73</sup> Moreover, Ed Creutz, the man who had hired Kohn at Carnegie Tech and who was now Vice President of Research at the General Atomics Division of the General Dynamics Corporation in San Diego, had recently concluded a consulting contract with him. This time, the allure was too great and Walter agreed to sign on. His only condition was that Keith Brueckner must serve as chair of the new department (KB85).

Walter's research group had grown to include three Ph.D. students and four postdoctoral fellows by the fall of 1959 when he submitted his resignation to the President of Carnegie Tech. His senior student, Vinay Ambegaokar, was one semester from graduation. His junior students, Larry Glasser and Edwin Woll, Jr., were not too far from the beginning of their research so Walter invited them to join him in La Jolla. Woll chose to accompany his advisor; Glasser remained in Pittsburgh and finished his degree with Assistant Professor J. Michael Radcliffe (LG13). Postdocs Hiroshi Hasegawa and Robert Howard had arrived the previous fall from Tokyo and Oxford, respectively, and worked together on a problem motivated by Kohn's experience with shallow donor states in semiconductors (Hasegawa 2003). Hasegawa accompanied Kohn to

<sup>72</sup> Langer and Vosko used a formulation of many-body perturbation theory due to Hubbard (1957).

<sup>73</sup> The regents of the University of California committed unprecedented financial resources so UCSD could recruit senior scientists like Kohn to its nascent faculty. In its first few years, 50 percent of new faculty hires at UCSD were made at the full professor level or above, as opposed to 15 percent for the University of California system as a whole (Kerr 2001).

San Diego while Howard moved on to a permanent position at the National Bureau of Standards in Washington, DC. Postdocs Emile Daniel and Anthony Houghton were former Ph.D. students of Jacques Friedel in Paris and Geoffrey Chester (in the group of Rudolf Peierls) in Birmingham, respectively. Both began research projects in metal alloy physics before moving to the west coast. Kohn himself taught a graduate course in advanced solid-state physics and gave a talk on “The Electron Theory of Solids” at a one-day “Solid-State Symposium” in New York City sponsored by the American Institute of Physics for the benefit of science writers from national magazines and newspapers.<sup>74</sup>

Even before leaving Pittsburgh, Walter worked hard to recruit faculty members to his new Physics Department in San Diego. He had immediate luck with three Bell Laboratories scientists, the statistical mechanician Harry Suhl, the nuclear magnetic resonance experimenter George Feher, and the superconductivity experimenter Bernd Matthias.<sup>75</sup> In an October 26, 1959, letter to Keith Brueckner, Kohn laments Quin Luttinger’s decision to choose Columbia University over UCSD and suggests several solid-state and/or low-temperature physicists whom Brueckner should approach.<sup>76</sup> On the theoretical side, he proposed J. Robert Schrieffer, the junior author of a breakthrough paper on the theory of superconductivity published in 1957, Volker Heine, a specialist in the electronic structure of metals from the University of Cambridge, and Philippe Nozières, an expert in many-body theory trained at Princeton by David Pines. On the experimental side, he suggested his old Harvard friend and magnetic resonance practitioner, Charles Slichter, and the liquid helium experts William Vinen and Russell Donnelly. As it turned out, none of these people joined the UCSD faculty.<sup>77</sup>

Kohn’s arrival in San Diego in January 1960 coincided with his election as a Fellow of the American Physical Society (APS), the professional organization of American physicists.<sup>78</sup> Resettlement and administrative issues dominated his time at first, so Kohn used his students, postdocs, and short-term visitors to pursue a research agenda now focused primarily on the physics of metals and alloys.<sup>79</sup> A new postdoctoral fellow, Stephen Nettel, studied the spatial arrangement of electron spins in the ground state of a *homogeneous and non-interacting electron gas*, a much-studied hypothetical system composed of a collection of mobile electrons (with their mutual Coulomb interaction turned off) distributed throughout a uniform and static distribution of elec-

<sup>74</sup> The symposium was organized by Conyers Herring from Bell Telephone Laboratories. Besides Kohn, the lecturers were John Fisher from the General Electric Research Laboratory, Jack Goldman from (by then) the Ford Motor Company Research Laboratory, and Frank Herman from RCA Laboratories. WKP. October 21, 1959, letter from Conyers Herring to Walter Kohn.

<sup>75</sup> Suhl and Feher arrived in San Diego in 1960. Matthias waited a year because “during the first year there will be too many administrative chores” (Feher 2002).

<sup>76</sup> WKP. October 26, 1959, letter from Walter Kohn to Keith Brueckner.

<sup>77</sup> Offers were also proffered to (and declined by) the French magnetic resonance expert, Anatole Abragam (Abragam 1989) and Kohn’s old Harvard friend Ben Mottelson, a nuclear physicist at Bohr’s Institute for Theoretical Physics. WKP. October 9, 1959, letter from Keith Brueckner to Ben Mottelson.

<sup>78</sup> An APS Fellow is judged by his peers to have made “exceptional contributions to the physics enterprise”. In 1960, the total number of Fellows was 1,653 out of a total society membership of 16,157 (AMP).

<sup>79</sup> A visiting French scientist, Jacques des Cloizeaux, arrived in the fall of 1960 and worked on a statistical mechanics problem.

trically neutralizing positive charge (Kohn and Nettel 1960). Emile Daniel and former postdoc Seymour Vosko used many-body perturbation theory to study the sharpness of the Fermi surface for a fully interacting electron gas at zero temperature, and Tony Houghton studied the specific heat and spin susceptibility of a dilute alloy (Daniel and Vosko 1960; Houghton 1961).<sup>80</sup> The numerical calculations of Daniel and Vosko confirmed Quin Luttinger's analytic demonstration that electron-electron interactions do not destroy the sharpness of the Fermi surface of an electron gas. This result was reported by Luttinger at a (retrospectively famous) meeting attended by Kohn and Vosko on "The Fermi Surface" held at Cooperstown, New York on August 22–24, 1960. (Luttinger 1960; Harrison and Webb 1960).

The La Jolla campus of the University of California opened for business in the fall of 1960. There were no undergraduates (until 1964), but sixteen physics graduate students arrived and began taking classes. Walter Kohn taught a course from 4:30 p.m. to 6:00 p.m. on Thursdays and from 9:30 a.m. to 11:00 a.m. on Saturdays using the textbooks *Thermodynamics* by Callen (1960) and *Elements of Statistical Mechanics* by ter Haar (1954).<sup>81</sup> On February 1, 1961, Kohn flew to New York City to attend the annual joint meeting of the American Physical Society and the American Association of Physics Teachers. He was there to accept the 1961 Oliver Buckley Solid State Physics Prize "for having extended and elucidated the foundations of the electron theory of solids" (Anonymous 1961). This prize, endowed in 1952 by Bell Telephone Laboratories and named in honor its former president and board chairman, is awarded each year by the APS to "recognize and encourage outstanding theoretical or experimental contributions to solid-state physics". Some measure of the esteem carried by this honor may be judged from the fact that four of the eight persons who won the Buckley Prize before Kohn later won a Nobel Prize (William Shockley, John Bardeen, Clifford Shull, and Nicolaas Bloembergen).

Sometime in the spring of 1961, Keith Brueckner announced that he was stepping down as the chair of the Physics Department after 1 year of service. He had accepted the position of vice president and technical director of the Institute for Defense Analyses in Washington, DC (KB94). Therefore, against his expressed desire and much to his chagrin, Walter Kohn found himself in the position of chair for the 1961 fall semester. As a department head at a new university, Kohn enjoyed opportunities and faced challenges that do not ordinarily arise for administrators at established universities. He was permitted to hire a dozen new faculty members (which doubled the size of his department), but the offices and laboratories he could offer new recruits occupied temporary space that would soon revert to the Scripps Institution of Oceanography. One interesting hire was his friend Norman Rostoker, who had turned himself into a plasma physicist at General Atomics since he and Walter had collaborated at Carnegie Tech. The senior faculty members recruited by Brueckner and Kohn had excellent research records, but many came from industrial or government laboratories with no teaching experience. It was Walter's responsibility to ensure that competent instructors

<sup>80</sup> A "sharp" Fermi surface has the property that a quantum state labeled by the quantum number wave vector  $\mathbf{k}$  is occupied by an electron if that wave vector lies inside the volume of the  $\mathbf{k}$ -space enclosed by the Fermi surface and unoccupied if  $\mathbf{k}$  lies outside that volume.

<sup>81</sup> The unusual hours were chosen for "the convenience of students employed in industry" (UCSDA).

**Fig. 8** Walter Kohn at age 39 (1962). Courtesy of Walter Kohn and the John Simon Guggenheim Foundation



staffed the courses offered to the first few classes of graduate students. At the same time, he maintained a research group of never less than five persons (graduate students, postdoctoral fellows, and visitors), served as an Associate Editor of the *Journal of Mathematical Physics*, team-taught a course on “Advanced Solid State Physics,” presented a university-wide lecture on “New Viewpoints in the Theory of Matter,” and submitted four research papers.<sup>82</sup>

Within his group, Edwin Woll, Jr., Kohn’s Ph.D. student from Carnegie Tech was making good progress with semi-quantitative calculations of Kohn’s phonon anomaly in the metals aluminum, sodium, and lead. Walter also began working with Michael Greene and Max Luming, two Ph.D. candidates from the 1960 crop of UCSD graduate students, and Chanchal Majumdar, a student from the 1961 class. Greene was tasked to use scattering theory to compute the resistivity of liquid alkali metals. Max Luming involved himself in calculations of the orbital susceptibility of dilute metal alloys but switched to theoretical particle physics after the publication of Kohn and Luming (1963).<sup>83</sup> Majumdar began a project on the theory of positron annihilation in metals. Overall, Kohn acquired a reputation among potential theory students as a supervisor with very high standards who could assign a thesis problem that might take a very long time to complete (PF13) (Fig. 8).

At the beginning of the fall 1962 semester, Walter learned that his colleague Norman Kroll would take over as Physics chair beginning in the fall 1963 semester. Immediately, he made an application to the John Simon Guggenheim Memorial Foundation for funds to support a recuperative leave for the fall 1963 semester (Hohenberg et al. 1990). His plan was to spend that time at the Physics Department of the École Normale Supérieure in Paris (GF62). This was an ideal place to get back to full-time research. It was also an ideal place to renew his personal and scientific ties with three specialists

<sup>82</sup> Kohn taught semiconductor physics and the transport and optical properties of metals for 5 weeks in the fall of 1962. His April 1962 campus-wide lecture was part of a series delivered by senior UCSD professors from various departments (LB13).

<sup>83</sup> Luming (later Luming Ren) switched his Ph.D. supervisor from Kohn to Assistant Professor David Wong because he felt that particle physics was “more fundamental” than solid-state physics (MR13).

in his own field of theoretical solid-state physics: Jacques Friedel, Pierre-Gilles de Gennes, and Philippe Nozières.

Kohn's fellowship application proposed that he would study the interaction of electrons and phonons in metals (GF62). This was a hot topic. The collisions between electrons and the particle-like phonons had long been recognized as important for a proper description of the electrical conductivity of metals (Ziman 1960). However, only 5 years earlier, John Bardeen, Leon Cooper, and J. Robert Schrieffer had proposed a many-electron wave function for a *superconductor* based on a model where the electron–phonon interaction mediates an effective attractive interaction between pairs of electrons with opposite spin (Bardeen et al. 1957). Moreover, barely a year earlier, neutron scattering experiments had confirmed Kohn's own prediction of anomalies in the phonon spectra of metals (Kohn 1959c). Accordingly, Kohn proposed to spend the fall of 1963 generalizing the theory of Kohn anomalies. For good measure, he also proposed to develop a theory of the effect of electron–phonon interactions on the optical properties of metals.

The Guggenheim Foundation responded positively to Walter's application in the spring of 1963. This news must have been a great stimulant because he quickly completed a calculation which achieved "a new and more comprehensive characterization of the insulating state of matter" (Kohn 1964). The fundamental difference between the conducting state and the insulating state had been an issue for Kohn since his Bell Labs inspired work with Luttinger on electrical transport (Kohn and Luttinger 1957; Luttinger and Kohn 1958). Subsequent papers on the behavior of a point charge in a dielectric, the nature of Wannier's spatially localized states in solids, and the electromagnetic properties of insulators continued this theme (Kohn 1958, 1959a; Ambegaokar and Kohn 1960). His new work took seriously a suggestion by Nevill Mott (1949) that the many-body wave function of an insulator should be fundamentally different from the many-body wave function of a conductor. Kohn exploited a groundbreaking paper that focused attention on the gauge principle for the electromagnetic vector potential in quantum mechanics (Aharonov and Bohm 1959) and used a characteristically elegant method to calculate the electrical conductivity of a ring threaded by a line of magnetic flux. The result was a proof that the spatial organization of the electrons in an insulator corresponds to a many-body wave function that breaks up into disconnected regions that do not overlap with one another. The published paper, Kohn (1964), has been called a "a mine of ideas and methods" by no less an expert than Walter's old Harvard classmate and Bell Laboratories colleague Philip Anderson (PA99).<sup>84</sup>

Now 40 years old, Walter Kohn was a mature solid-state physicist whose scientific talent and taste in problems had produced results that were highly valued by his peers. Two of those peers, David Pines and Charles Kittel, highlighted Kohn's work four and eight times, respectively, in their (now classic) 1963 graduate level textbooks *Elementary Excitations in Solids* and *Quantum Theory of Solids*. By the end of that

<sup>84</sup> Philip Warren Anderson (b. 1923) earned his Ph.D. in 1949 under the supervision of John van Vleck at Harvard University. He worked at Bell Telephone Laboratories before moving to Princeton University in 1954. He shared the 1977 Nobel Prize in Physics with Nevill Mott and John Van Vleck for "fundamental theoretical investigations of the electronic structure of magnetic and disordered systems" (PA77).

summer, Walter's manuscript on the "Theory of the Insulating State" was ready for submission, and he had only to review some professional correspondence before he could depart for Paris. In retrospect, the most important letter on his desk came from Lu Jeu Sham, a graduating Ph.D. student from John Ziman's group at the University of Cambridge whom Kohn had earlier recruited to become a postdoctoral fellow. Kohn had written to Sham to inform him about his Paris sabbatical and to urge him to come to San Diego as originally planned. Kohn proposed that Sham work on liquid metals with graduate student Mike Greene until he (Kohn) returned to campus. The return letter from Sham agreed to this plan.<sup>85</sup>

#### 4 Alloys in Paris

Walter Kohn's base of operations in Paris was the Ecole Normale Supérieure, one of the elite *grandes écoles* of the higher education system in France. His host was the 31-year-old Philippe Nozières, an expert in many-body theory who had just collaborated with Joaquin Luttinger to derive Landau's theory of the Fermi liquid using diagrammatic perturbation theory (Nozières and Luttinger 1962; Luttinger and Nozières 1962).<sup>86</sup> Walter began his research activities, but he did not work on the electron–phonon interaction as he had proposed to the Guggenheim Foundation. Some months earlier, he had changed his mind and decided to think more deeply about the electronic structure of disordered metal alloys. More precisely, he asked himself how one might best describe the behavior of the electrons in a bulk metal composed of different types of atoms where there is at least some randomness in the identities of the atoms that occupy the sites of the underlying periodic lattice.<sup>87</sup>

Unlike most theoretical solid-state physicists in the United States, Kohn had followed developments in alloy physics for more than a decade because of the intense experimental interest in this subject by his faculty colleagues in the Physics and Metallurgy Departments at Carnegie Tech. On the other hand, his personal contribution to the field consisted of only two published papers and both concerned *dilute* alloys like  $A_xB_{1-x}$  where the fraction  $x$  of A-type atoms dissolved in a host metal made of B-type atoms was very small (Kohn and Vosko 1960; Kohn and Luming 1963). He now turned his attention to *concentrated* alloys where the populations of A-type atoms and B-type atoms could be comparable. Philippe Nozières was not particularly interested in alloys (he was working on liquid helium at the time), but a short 30 km train ride took Kohn to the suburban campus of the University of Paris in Orsay where his old friend Jacques Friedel maintained his research group. Friedel was an acknowl-

<sup>85</sup> WKP. June 10, 1963, letter from Lu Jeu Sham to Walter Kohn.

<sup>86</sup> Philippe Nozières (b. 1932) graduated from the Ecole Normale Supérieure (ENS) in 1955 and earned his Ph.D. 2 years later from the University of Paris, albeit under the supervision of David Pines at Princeton University. He spent a decade at the ENS before moving to the Institut Laue-Langevin (ILL) in Grenoble. He also lectures at the Collège de France in his capacity (since 1983) as Professor of Statistical Physics (Nozières 2012).

<sup>87</sup> In July, Kohn had written to an editor at Academic Press confirming his interest to contribute to a book about "Impurities in Metals" and indicating that he would be "working in this field" during his stay in Paris. WKP. August 6, 1963, letter from Alan R. Liss (Vice President, Academic Press, Inc.) to Walter Kohn.

edged expert in the theory of metals and alloys.<sup>88</sup> Also present in Orsay at the time were André Guinier, an experimentalist renowned for his X-ray diffraction studies of alloys, and Pierre-Gilles de Gennes, a theorist working on a set of problems he would soon collect and discuss in his book, *Superconductivity in Metals and Alloys* (1966).<sup>89</sup>

Kohn immersed himself in the literature of metals and alloys and soon discovered that two seemingly contradictory points of view dominated discussions of their electronic structure. I pause here to sketch the field as he found it, because his desire to reconcile these points of view was the immediate trigger for the creation of density functional theory. The fundamental problem was to calculate the eigenfunctions and energy eigenvalues for a binary alloy where A-type atoms replace a fraction of the atoms in a perfect B-type crystal. If the replaced B-type atoms are chosen randomly, the resulting structure is no longer periodic and the Bloch theorem which underlies conventional band-structure theory is no longer valid.<sup>90</sup> By the end of the 1950s, approximate ways to analyze this situation had been proposed by Nordheim (1931), Jones (1934), and Friedel (1954). All of them acknowledge a debt to the eminent English physical metallurgist William Hume-Rothery and his 1931 book, *The Metallic State*.

The first half of Hume-Rothery (1931) reviews years of experimental effort to systematize the electric, thermoelectric, and thermionic properties of metals and alloys. The second half reviews the classical and quantum mechanical theories that had been devised to explain some of these properties. A typical result reported in *The Metallic State* was the observation that many disordered substitutional alloys  $A_xB_{1-x}$  exhibit an electrical resistivity that varies with the A-type atom concentration as  $x(1 - x)$ . Nordheim (1931) explained this by replacing the real alloy, where dissimilar potentials  $V_A(r)$  and  $V_B(r)$  act on the valence electrons near lattice sites occupied by A-type atoms and B-type atoms, respectively, by a fictitious *virtual crystal* where the valence electrons near every lattice site feel the same average potential,  $\bar{V}(r) = xV_A(r) + (1 - x)V_B(r)$ . By construction, the potential energy function for the virtual crystal is periodic and any band-structure method becomes applicable to find the eigenfunctions and energy eigenvalues (Muto 1938).

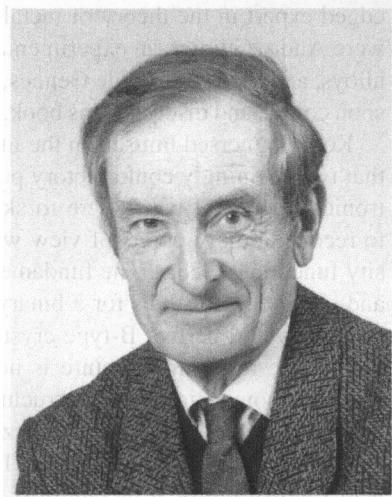
Jones (1934) was concerned with some empirical “rules” deduced by Hume-Rothery which related the crystal structure of certain alloys to their “electron concentration,” i.e., the ratio of the total number of valence electrons to the total number of atoms in the entire crystal. Jones focused on the dilute limit and made two indepen-

<sup>88</sup> Jacques Friedel (b. 1921) is a fourth-generation French scientist who was educated at the École Polytechnique (1944–1946) and the École Nationale Supérieure des Mines (1946–1948) before earning his Ph.D. in 1952 under the supervision of Nevill Mott at the University of Bristol. Friedel began his academic career at the Sorbonne, but moved in 1959 to the Orsay campus of the University of Paris, now the University of Paris-Sud. Friedel’s life-long interests in metallurgy and the physics of metals resulted in over 200 theoretical publications, most of them characterized by the use of simple models and elementary mathematics. Kohn and Friedel met at a July 1953 Gordon Conference in Laconia, New Hampshire devoted to the Chemistry and Physics of Metals (Kohn 2012).

<sup>89</sup> Pierre-Gilles de Gennes (1932–2007) changed fields after the publication of his superconductivity book and won the 1991 Nobel Prize in Physics for his work on the statistical physics of liquid crystals and polymers.

<sup>90</sup> Alloys of this kind are called *disordered*. The Bloch theorem remains valid for *ordered alloys* where the A-type atoms form a spatially periodic structure of their own.

**Fig. 9** Jacques Friedel pioneered a spatially local description of the electronic structure of alloys. Courtesy of the AIP Emilio Segrè Visual Archive



dent assumptions. First, he used a *nearly free electron* description where the energy spectrum and wave functions of the host B-type metal was presumed to differ only slightly from the energy spectrum and wave functions of a collection of completely free electrons. Second, he made a *rigid-band* approximation which supposed that the sole effect of the A-type atoms was to contribute their valence electrons to the pre-existing “sea” of valence electrons contributed by the B-type atoms. This implied that the electronic structure of the alloy was identical to the electronic structure of the host metal except that a few energy states were occupied (empty) in the alloy compared to the host if the valence of the A-type atoms was larger (smaller) than the valence of the B-type atoms.<sup>91</sup> Using quantum mechanical perturbation theory, Jones estimated the change in total electronic energy when the Fermi surface of the rigid-band alloy contacts the Brillouin zone boundary for different crystal structures. In this way, he was able to rationalize the Hume-Rothery’s electron concentration rules in a semi-quantitative way.

The virtual crystal and rigid-band approximations share a “delocalized” view of the electrons in a metal alloy. This means that each electron in the conduction band occupies an eigenstate whose Bloch-like wave function has a nonzero amplitude on every atomic site of the alloy [see the left side of Eq. (5)]. This perspective gained popularity among practitioners because its successes were detailed in the first two research monographs devoted exclusively to metal physics: *The Theory of Metals* (1936) by Alan Wilson and *The Theory of the Properties of Metals and Alloys* (1936) by Nevill Mott and Harry Jones.

A rather different, “localized” point of view was developed by Friedel (1954) (Fig. 9). He considered an alloy where  $\Delta Z_V$  is the valence difference between the solute A-type atoms and the solvent B-type atoms and recognized that each A-type

<sup>91</sup> This follows from the eigenstate occupation rules of quantum mechanics which dictate that states are populated by electrons in order of increasing energy beginning with the lowest.

atom with its valence electrons removed amounts to a point-like impurity with charge  $\Delta Z_V$  with respect to the host crystal. The screening of this impurity [discussed earlier in connection with the work of Langer and Vosko (1959)] by the entire sea of conduction electrons implies that electronic charge density accumulates in the immediate vicinity of the A-type atoms. The delocalized electrons of the host scatter from these local charge accumulations and Friedel used perturbation theory to show that the energy shift of each scattering state (with respect to the Fermi energy) was the same as the energy shift predicted by the rigid-band model. He went on to use this "local" perspective to rationalize other experimental trends summarized in Hume-Rothery's book. An even more localized, covalent bond approach to metals was advocated by Pauling (1949).

The semi-quantitative nature of all existing theories of alloy electronic structure was criticized by John Slater at an October 1955 conference devoted to the theory of alloy phases.<sup>92</sup> Speaking to an audience of physicists, physical chemists, metallurgists, and crystallographers, Slater opened the conference by remarking that (Slater 1956)

The metallurgist expects the physicist to be able to apply wave mechanics to the problem of the cohesive energy of metals. By this one means the energy of the metal as a function of the positions of the nuclei...Unfortunately, the errors in our present calculations of the energies of the isolated atoms and of the atoms combined into a metallic crystal are both considerably larger than the energy difference between the two, which is the cohesive energy which we hope to find...This theory is not yet in a position to make calculations of the accuracy which the metallurgists need and which they have been led to believe that they have been getting. Metallurgists have been understandably anxious to get real guidance from physicists regarding their problems. A few papers written by theoreticians have led them to think that this guidance could be actually given in a quantitatively satisfactory form. For instance, a large literature has grown up as a result of papers [published] in the middle 1930s by Jones...and Pauling has discussed metallic cohesion and ferromagnetism using methods that seem simple and quantitative. I wish to state my very firm opinion that these theories, as far as they pretend to be quantitative, are based on approximations which are not really justified. They may have qualitative truth in them, but they do not represent quantitative conclusions firmly based on fundamental theory.

It is perhaps unsurprising that Slater's research group at the time was exploring the quantitative accuracy of his own "augmented plane wave" method for band-structure calculations (Slater 1953).

<sup>92</sup> John Clarke Slater (1900–1976) was the chair of the Physics Department at the Massachusetts Institute of Technology (MIT) from 1930 to 1951. He wrote an experimental Ph.D. thesis at Harvard and then traveled to Europe where he made several important theoretical contributions to the early development of quantum mechanics. Dissatisfaction with "formal theory" led him to develop a large research group at MIT devoted to solving the Schrödinger equation numerically to calculate the physical properties of atoms, molecules, and solids. It was Slater's book *Introduction to Chemical Physics* that was purchased and read by the young Walter Kohn while he awaited release from internment in wartime Canada (Morse 1982).

In Paris in the fall of 1963, Walter Kohn was in an excellent position to learn the latest developments in both the localized and delocalized approaches to alloy theory. The preceding January, Jacques Friedel and André Guinier had completed editing *Metallic Solid Solutions*, a book which documented the proceedings of an international symposium on the electronic and atomic structure of alloys held in Orsay in July 1962.<sup>93</sup> In one invited paper, Stanley Raimes of Imperial College noted that Fermi surface measurements for the noble metals invalidated the nearly free electron assumption used by Jones (1934), but did not quash the rigid-band approximation itself (Raimes 1963). Similarly, an invited paper by Frank Blatt of Michigan State University asserted that a broad range of transport measurements showed that “the rigid-band model is a good approximation to the electronic structure of dilute alloys” (Blatt 1963). On the other hand, Blatt continued, “it is difficult to overstate the importance” of Friedel’s local screening model for the interpretation of not only resistivity and thermoelectric data for alloys, but also for data obtained from measurements of impurity diffusion, positron annihilation, and the Knight shift”. Friedel himself reported an extension of his previous work to the case of transition-metal atom impurities where screening occurs by the occupation of atomic-like orbitals spread out in energy into “virtual bound-state resonances” (Friedel 1963).

The most general conclusion to be drawn from the papers collected in *Metallic Solid Solutions* was that some observations were best understood assuming that the conduction electrons of an alloy are delocalized through the volume of the crystal while other observations were best understood assuming that the most relevant electrons are localized in the immediate vicinity of the solute atoms. At least two prominent metallurgists regarded these points of view as complementary rather than contradictory. In the fourth edition of their *Structure of Metals and Alloys*, William Hume-Rothery and Geoffrey Vincent Raynor write (Hume-Rothery and Raynor 1962)

The covalency interpretation and the Brillouin zone picture each express a part of the truth. In the case of the diamond structure, for example, the covalency theory...gives the more correct picture of the probable cloud density of valence electrons in the crystal. This concept by itself ignores the fact that electrons are free to move in the crystal, and this freedom is emphasized by the zone theories, which in their turn ignore the variation of the electron-cloud density in space. Both concepts are required to express the whole truth.

The complementarity expressed by this paragraph was well known to many solid-state physicists, and particularly so to Walter Kohn who had published a fundamental paper on the relationship between the delocalized Bloch functions and the localized Wannier functions (Kohn 1959a). Kohn had also kept up with band-structure calculations and could well appreciate the point John Slater had made about the absence of quantitative calculations in alloy theory (Callaway and Kohn 1962).

Kohn has written about his 1963 survey of the alloy literature on several occasions. His 1990 account, which is closest in time to the actual events, recalls the “rough

<sup>93</sup> The unedited proceedings of this conference were also published in the October 1962 issue of *Journal de Physique et le Radium*. Reading them may have been the trigger for Kohn to change the subject of his Paris research from the electron–phonon interaction to alloy physics.

and ready” rigid-band model and then recounts a calculation of the total energy of a disordered alloy (Hohenberg et al. 1990). This is interesting because the total energy of a real metal was not a focus of research at the time. Indeed, the only paper in *Metallic Solid Solutions* concerned with total energy begins with the statement (Cohen 1963),

In the early history of the theory of metals, calculation of the cohesive energy was a central concern. Apart from very considerable development of the theory of the electron gas, recent effort, both experimental and theoretical, has been focused primarily on properties of one-electron character. In the present work, we have returned to the study of the cohesive energy of metals.

The remainder of this paper, written by Walter’s friend Morrel Cohen from the University of Chicago, displays an exact formula for the total energy of a uniform (constant density) electron gas due to Nozières and Pines and then generalizes it to the case of an arbitrary “non-uniform system”. Both formulae involve an integral over a parameter  $\lambda$  with the quantities in the integrand computed assuming a charge on the electron of  $\lambda e$ . The limits of the integral extend from  $\lambda = 0$  (the non-interacting electron gas) to  $\lambda = 1$  (the fully interacting electron gas).

In his 1990 reconstruction, Kohn wrote a similar integral to compute  $\Delta E$ , the difference in total energy between a real  $A_xB_{1-x}$  alloy and the same alloy in the virtual crystal approximation. If  $Z^A$  and  $Z^B$  are the atomic numbers of the A-type and B-type atoms, every ion in the virtual crystal has nuclear charge  $\bar{Z} = xZ^A + (1-x)Z^B$ . Then, replacing  $\Delta Z = Z^A - Z^B$  by  $\lambda \Delta Z$ , Kohn evaluated the integral of  $dE/d\lambda$  from  $\lambda = 0$  to  $\lambda = 1$  to second order in  $\Delta Z$  (keeping  $\bar{Z}$  fixed). The resulting expression for  $\Delta E$  depended on two quantities only: the electron density distribution of the virtual crystal,  $\bar{n}(\mathbf{r})$ , and the electron density distribution of the real alloy,  $n(\mathbf{r})$ . At this point, “the question occurred to Kohn whether a knowledge of  $n(\mathbf{r})$  alone determined—at least in principle—the total energy” (Hohenberg et al. 1990). In other words, could the many qualitative successes of the Friedel point of view, which put great emphasis on the space-varying electronic charge density inside an alloy, be elevated to show that the exact charge density uniquely predicts the exact total energy?<sup>94</sup>

It is important to understand the revolutionary nature of this question. Notwithstanding the work of Cohen mentioned above, most solid-state theorists in the early

<sup>94</sup> In later recollections, Kohn emphasizes the concept of charge transfer in alloys. His Nobel Prize autobiography reports that he read some “metallurgical literature in which the concept of an effective charge  $e^*$  of an atom in an alloy was prominent, which characterized in a rough way the transfer of charge between atomic cells” (WK98). His Nobel Prize lecture notes similarly that “there is a transfer of charge between...unit cells on account of their chemical differences. The electrostatic interaction energies of these charges are an important part of the total energy. Thus, in considering the energetics of this system, there was a natural emphasis [in the literature] on the electron density distribution  $n(\mathbf{r})$ ” (Kohn 1999). Despite these remarks, I have been unable to find any significant discussion of charge transfer or “effective charge” in the pre-1963 literature of metallurgy or metal physics. Indeed, if they mention this type of charge transfer at all, review articles of the period consistently refer to the same two papers—one by Mott (1937) which concerns ordered alloys and one by Varley (1954) which demonstrates that the electrostatic energy associated with charge transfer is negligible in disordered alloys. On the other hand, less than 10 years after the events narrated here, charge transfer became an important variable in two proposed theories of binary alloy formation (Hodges and Stott 1972; Miedema et al. 1973). I have found no literature of the time that emphasizes the spatially varying electron density distribution  $n(\mathbf{r})$  in alloys except in the most qualitative terms (see the passage by Hume-Rothery and Raynor quoted earlier in this section).

1960s thought about the total energy of a solid along the lines laid out by Frederick Seitz in his widely admired textbook, *The Modern Theory of Solids* (1940). One starts with the nuclear charge  $eZ_k$  and the fixed position  $\mathbf{R}_k$  of each of the  $M$  nuclei in the system. The Coulomb potential energy of interaction between pairs of nuclei is a classical quantity which poses no problem to compute. The remaining energy terms all contribute to the Schrödinger equation for the  $N$ -electron wave function: the kinetic energy of the electrons, the Coulomb potential energy of interaction between every pair of electrons, and the Coulomb potential energy of interaction between every electron and every nucleus.

It will be convenient to define  $v(\mathbf{r})$  as the potential energy of interaction between an electron at the point  $\mathbf{r}$  and all the fixed nuclei:

$$v(\mathbf{r}) = -e^2 \sum_{k=1}^M \frac{Z_k}{|\mathbf{r} - \mathbf{R}_k|}. \quad (7)$$

This potential energy appears in the Schrödinger equation, as do the operators for the electron kinetic energy and the electron-electron potential energy,

$$\hat{T} = -\frac{\hbar^2}{2m} \sum_{k=1}^N \nabla_k^2 \quad \text{and} \quad \hat{U} = \frac{1}{2} \sum_{k=1}^N \sum_{m=1}^N \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_m|}. \quad (8)$$

The Schrödinger equation determines the  $N$ -electron wave function,  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ , and then the electron density distribution,

$$n(\mathbf{r}) = \int \psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \cdots d\mathbf{r}_N. \quad (9)$$

If we omit the classical ion-ion energy, which does not involve the electrons, the total energy is

$$E = \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + \langle \psi | \hat{T} | \psi \rangle + \langle \psi | \hat{U} | \psi \rangle, \quad (10)$$

where the last two terms are expressed as averages (expectation values) with respect to the ground-state wave function.

The conventional perspective outlined in the previous paragraph shows that the external potential,  $v(\mathbf{r})$ , is the only term in the Schrödinger equation which distinguishes one alloy from another. Therefore,  $v(\mathbf{r})$  determines the wave function from the Schrödinger equation, which in turn determines the electron density  $n(\mathbf{r})$  from Eq. (9) and the total energy  $E$  from Eq. (10). From this point of view, the energy amounts to a *functional* of the external potential. Of course, the accuracy of the computed energy depends on the quality of the choice made for the form of the  $N$ -electron wave function used to solve the Schrödinger equation.

Kohn now contemplated a radical inversion of this procedure. Was it possible that the total energy depended only on the electron density  $n(\mathbf{r})$ ? That is, could the total energy be a functional of the density alone? If so, knowledge of  $n(\mathbf{r})$  was sufficient to determine (implicitly) the external potential, the  $N$ -particle wave function, and all the

ground-state properties, including the Green functions of many-body theory! This was a very deep question. Walter realized he was not doing alloy theory anymore (WK12).

## 5 The work of Hohenberg and Kohn

Kohn's proposition that the total energy of an electron system was a functional of the density seemed preposterous on the face of it. How could knowledge of the electron density, which is a function of 3 variables, be sufficient to compute the total energy when the last two terms in Eq. (10) depend explicitly on the many-electron wave function, which is a function of  $3N$  Cartesian variables? Looking for support, Walter asked himself whether he knew *any* examples where complete knowledge of  $n(\mathbf{r})$  implied complete knowledge of  $v(\mathbf{r})$  (Hohenberg et al. 1990). One such example was the elementary Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + [v(\mathbf{r}) - E]\psi(\mathbf{r}) = 0. \quad (11)$$

One can always choose  $\psi(\mathbf{r})$  real for this equation. Therefore, the electron density is  $n(\mathbf{r}) = \psi^2(\mathbf{r})$  and the inversion we seek is a matter of algebra:

$$v(\mathbf{r}) = E + \frac{\hbar^2}{2m} \frac{\nabla^2 \sqrt{n(\mathbf{r})}}{\sqrt{n(\mathbf{r})}}. \quad (12)$$

Unfortunately, Eq. (11) applies only to a one-particle system and thus does not shed any light on the many-body problem. A more relevant example known to Kohn was the Thomas–Fermi method, a semi-classical but self-consistent approximation to the quantum theory of a many-electron system with a non-uniform density  $n(\mathbf{r})$  (March 1975; Zangwill 2013). Nevill Mott had used this method to calculate the screening of a point charge by the conduction electrons in a metal. For the problem considered here, Thomas–Fermi theory method shows that  $n(\mathbf{r})$  determines  $v(\mathbf{r})$  through the relation<sup>95</sup>

$$v(\mathbf{r}) = E - \frac{1}{2m} \left( \frac{3\hbar^3}{8\pi} \right)^{2/3} n^{2/3}(\mathbf{r}) - e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (13)$$

Encouraged by these examples, Kohn sought to prove that *the ground-state electron density  $n(\mathbf{r})$  uniquely determines the external potential  $v(\mathbf{r})$* . Such a simple result (if true) could not depend on the details of the many-electron wave function. Therefore, he looked for a very general idea to exploit and found it with the Rayleigh–Ritz variational principle (Hohenberg et al. 1990). The reader will recall that this was the first tool Walter had placed in his theoretical toolbox while still a student at the University of Toronto. The *reductio ad absurdum* proof is “disarmingly simple” (Parr and Yang 1989).

<sup>95</sup> The coefficient of the kinetic energy term in Eq. (13) includes the electron mass  $m$  and Planck's constant  $\hbar$ .

Assume that a Hamiltonian (energy) operator  $\hat{H} = \hat{v} + \hat{T} + \hat{U}$  produces a ground-state energy  $E_0$ , a ground-state wave function  $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$  and an electron density  $n(\mathbf{r})$ . Contrary to what we wish to prove, assume that another Hamiltonian  $\hat{H}' = \hat{v}' + \hat{T} + \hat{U}$  produces a ground-state energy  $E'_0$ , a ground-state wave function  $\psi'(\mathbf{r}_1, \dots, \mathbf{r}_N)$ , but the *same* electron density  $n(\mathbf{r})$ . The idea is to use  $\psi'$  as a trial function in the variational principle for  $\hat{H}$  in Eq. (1). Ignoring the possibility of degeneracy, this gives the strict inequality<sup>96</sup>

$$E_0 < \langle \psi' | \hat{H} | \psi' \rangle = \langle \psi' | \hat{H}' | \psi' \rangle + \langle \psi' | \hat{H} - \hat{H}' | \psi' \rangle = E'_0 + \int n(\mathbf{r}) [v(\mathbf{r}) - v'(\mathbf{r})] d\mathbf{r}. \quad (14)$$

Similarly, we may use  $\psi$  as the trial function in the variational principle for  $\hat{H}'$ . The result is the same as Eq. (14) with the primed and unprimed variables exchanged:

$$E'_0 < \langle \psi | \hat{H}' | \psi \rangle = \langle \psi | \hat{H} | \psi \rangle + \langle \psi | \hat{H}' - \hat{H} | \psi \rangle = E_0 + \int n(\mathbf{r}) [v'(\mathbf{r}) - v(\mathbf{r})] d\mathbf{r}. \quad (15)$$

Adding Eqs. (14)–(15) yields  $E_0 + E'_0 < E'_0 + E_0$ , which is impossible. Hence, our assumption that two external potentials correspond to the same electron density is false.

Kohn was exhilarated by his proof, but “it seemed such a remarkable result that I did not trust myself” (WK98). He looked around for help and found it in the person of Pierre Hohenberg (Fig. 10). Hohenberg had just arrived in Paris after completing a postdoctoral year doing many-body theory with Alexei Abrikosov and Lev Gor’kov in Moscow, but was having trouble getting the attention of Nozières, his new postdoctoral supervisor (PH12). Walter proposed that they work together and Pierre agreed. Like Kohn’s previous collaborators, Res Jost and Quin Luttinger, Hohenberg was a rather formal theoretical physicist. He had been trained at Harvard by Paul Martin and his 1962 Ph.D. thesis, “Excitations in a dilute condensed Bose gas,” used density matrix and Green function methods to provide microscopic justification for phenomenological theories that had been offered by Lev Landau and others to explain the properties of superfluid helium.

Hohenberg’s first task was a literature search to discover whether the theorem Kohn had proved was already known. Apparently not. However, it had been known for about a decade that a computation of the total energy of a system of nuclei and electrons did not really require complete knowledge of the entire  $N$ -particle wave function (Löwdin 1959; McWeeny 1960; Coleman 1963). It was sufficient to specify a quantity derived from the wave function called the *second-order density matrix*.<sup>97</sup> In principle, there exists a variational principle for the energy where the second-order density matrix is varied rather than the wave function. Unfortunately, it was not known what properties

<sup>96</sup> Later analysis showed that removing the assumption of no degeneracy does not invalidate the final result (Parr and Yang 1989).

<sup>97</sup> Another necessary quantity, the first-order density matrix, is derivable from the second-order density matrix.

**Fig. 10** Pierre Hohenberg in 1965, soon after his work with Kohn on density functional theory. Courtesy of Pierre Hohenberg



the density matrix had to possess to ensure that it was derivable from an  $N$ -particle wave function. This became known as the “ $N$ -representability problem”.

In a similar way, Kohn’s theorem reminded Hohenberg of “formal work on stationary entropy and renormalization which had just been completed by Paul Martin and Cyrano de Dominicis, also working together in Paris” (Hohenberg et al. 1990). These authors had studied the grand partition function of an arbitrary many-body system and used the mathematical technique of Legendre transformations to effect the desired “renormalizations”. The latter eliminated the functional dependence on any one-body potential (like the external potential above) in favor of functional dependence on a one-particle distribution function. It also eliminated the functional dependence on any two-particle potential (like the Coulomb interaction between pairs of electrons) in favor of functional dependence on a two particle distribution function (Dominicis 1963; de Dominicis and Martin 1964). Fifty years later, Hohenberg and Kohn differ slightly in their recollection of whether Legendre transformations played any role in their work together. Kohn recalls that he and Hohenberg recognized that his theorem could be interpreted as a Legendre transformation only after the fact and notes that the final published paper makes no mention of it (WK13b). Hohenberg recalls that (PH12)

we were certainly thinking in the language of Legendre transformations, but we did not need that idea in the end. It was characteristic of Walter’s style to introduce [in print] only those theoretical ideas needed to solve the problem at hand.

Martin had returned to Harvard, but de Dominicis worked at the Centre d’Etudes Nucléaires in nearby Saclay. According to Hohenberg, “it took a number of intense but informative discussions with de Dominicis and his colleague Roger Balian to convince them that the procedure worked with the density rather than the distribution function (Hohenberg et al. 1990)”. Philippe Nozières finally joined the conversation when he

learned of the larger theoretical issue that now engaged Hohenberg and Kohn. As he later recalled (PN12),

The three of us discussed it a lot. But I was not fully convinced. In my opinion, putting all the emphasis on the density did not account properly for exchange and correlations. I did not share the enthusiasm of Walter and Pierre and I stayed aside.

Accordingly, Hohenberg and Kohn proceeded on their own to the natural next step: a reformulation of the Rayleigh–Ritz variational principle in terms of the density rather than the many-body wave function.

Kohn’s theorem implies that the many-body wave function is a functional of the ground-state electron density  $n(\mathbf{r})$ . The same is true of the exact kinetic energy  $T[n]$  and the exact electron–electron potential energy  $U[n]$ . Therefore, if

$$F[n] = T[n] + U[n] \quad (16)$$

is the sum of these two, the total energy in Eq. (10) is

$$E[n] = \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F[n]. \quad (17)$$

Now, let  $n_T(\mathbf{r}) \geq 0$  be a *trial density* which produces the correct total number of electrons,  $N = \int n_T(\mathbf{r}) d\mathbf{r}$ . By Kohn’s theorem, this density determines its own external potential, Hamiltonian, and ground-state wave function  $\psi_T$ . In that case, the usual wave function variational principle expressed by Eq. (1) tells us that

$$\langle \psi_T | \hat{H} | \psi_T \rangle = \int n_T(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F[n_T] = E[n_T] \geq E[n]. \quad (18)$$

The variational principle in Eq. (18) establishes that the energy in Eq. (17) evaluated with the true ground-state density is minimal with respect to all other density functions for the same number of particles.

The proofs given just above appear early in Hohenberg and Kohn (1964), the first foundational paper of density functional theory. In connection with Eq. (18), Hohenberg and Kohn (HK) use a footnote to warn the reader of a possible “v-representability problem” because “we cannot prove whether an arbitrary positive definite distribution  $n(\mathbf{r})$  which satisfies  $\int n(\mathbf{r}) d\mathbf{r} = N$  can be realized for *some* external potential”. They express confidence that all “except some pathological distributions” will have this property but the mere fact that they draw attention to this point demonstrates how carefully the authors looked for holes in their arguments.<sup>98</sup>

HK make a point to remark that the functional  $F[n]$  in Eq. (16) is “universal” in the sense that it is valid for any number of particles and any external potential. Even more significant for later work, they define yet another functional  $G[n]$  by extracting from

<sup>98</sup> The term “v-representability problem” was coined in 1975. See Parr and Yang (1989) and Kryachko and Ludeña (1990) for extensive discussion of this issue.

$F[n]$  the classical Coulomb energy of a system with charge density  $en(\mathbf{r})$ . Doing this renders Eq. (17) in the form

$$E[n] = \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + \frac{e^2}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + G[n]. \quad (19)$$

The functional  $G[n]$  in Eq. (19) includes the exact kinetic energy of the electron system and all the potential energy associated with the electron-electron interaction that is *not* already counted by the classical electrostatic energy. Needless to say, HK could not write down  $G[n]$ . Doing so would imply that they had solved the entire many-electron problem.

The approach Hohenberg and Kohn took to analyze  $G[n]$  reflects the way Kohn chose to frame the final published paper. There is no mention of the alloy problem or even of any desire to re-formulate the electronic structure problem for solids. Instead, the title of the HK paper is simply “Inhomogeneous electron gas” and the first line of the abstract announces that “this paper deals with the ground state of an interacting electron gas in an external potential  $v(\mathbf{r})$ ”. The introduction goes on to note that “during the last decade, there has been considerable progress in understanding the properties of a homogeneous, interacting electron gas”. A footnote refers the reader to David Pines’ book *Elementary Excitations in Solids* (1963) for the details. HK then remind the reader about the Thomas–Fermi method,

in which the electronic density  $n(\mathbf{r})$  plays a central role... This approach has been useful, up to now, for simple though crude descriptions of inhomogeneous systems like atoms and impurities in metals. Lately, there have been some important advances along this second line of approach... The present paper represents a contribution in the same area.

HK confirmed that the Thomas–Fermi model of electronic structure follows from Eq. (19) using an expression for  $G[n]$  which accounts approximately for the kinetic energy of the electrons but takes no account of the non-classical electron-electron potential energy. Specifically, the kinetic energy density at a point  $\mathbf{r}$  of the real system is set equal to the kinetic energy density of an infinite gas of *non-interacting* electrons with a uniform density  $n = n(\mathbf{r})$ . The latter is computed using elementary statistical mechanics and one finds (March 1975; Zangwill 2013)

$$G_{TF}[n] = \frac{3}{10m} \left( \frac{3h^3}{8\pi} \right)^{2/3} \int n^{5/3}(\mathbf{r}) d\mathbf{r}. \quad (20)$$

After inserting Eq. (20) into Eq. (19) to produce  $E_{TF}[n]$ , the variational principle in Eq. (18) directs us to minimize  $E_{TF}[n]$  with respect to density. This is done using Lagrange’s method to ensure that the total particle number,  $N = \int n(\mathbf{r}) d\mathbf{r}$ , remains constant. The final result is the Thomas–Fermi expression in Eq. (13).

The Thomas–Fermi model never went out of fashion as a quick and easy way to gain qualitative information about atoms, molecules, solids, and plasmas. By 1957, the British solid-state physicist Norman March was able to publish a 100-page review article surveying the successes and failures of the model and its generalizations (March

1957). Earlier, I labeled 1957 as the “magic year” when many-body Green functions and diagrammatic perturbation theory transformed the study of many-electron systems. Therefore, it is not surprising that several physicists—including Kohn’s old postdoctoral colleague Sidney Borowitz—applied these methods with the aim to systematically generalize the Thomas–Fermi model to include the effects of electron correlation and spatial inhomogeneity (Baraff and Borowitz 1961; DuBois and Kivelson 1962). These papers are among the “important advances” noted by HK in the passage quoted just above.<sup>99</sup>

As trained solid-state physicists, HK knew that the entire history of research on the quantum mechanical many-electron problem could be interpreted as attempts to identify and quantify the physical effects described by  $G[n]$ . For example, many years of approximate quantum mechanical calculations for atoms and molecules had established that the phenomenon of *exchange*—a consequence of the Pauli exclusion principle—contributes significantly to the potential energy part of  $G[n]$ . Exchange reduces the Coulomb potential energy of a system by tending to keep electrons with parallel spin spatially separated. The remaining potential energy part of  $G[n]$  takes account of short-range *correlation* effects. Correlation also reduces the Coulomb potential energy by tending to keep *all* pairs of electrons spatially separated. The effect of correlation is largest for electrons with antiparallel spins because these pairs are not kept apart at all by the exchange interaction. I note for future reference that the venerable Hartree–Fock approximation takes account of the kinetic energy and the exchange energy exactly but (by definition) takes no account of the correlation energy (Seitz 1940; Löwdin 1959; Slater 1963).

HK devoted the remainder of their time together to studying  $G[n]$  for two cases: (1) an interacting electron gas with a nearly constant density; and (2) an interacting electron gas with a slowly varying density. For the nearly constant density case, HK wrote  $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$  with  $\tilde{n}(\mathbf{r})/n_0 \ll 1$  and pointed out that  $G[n]$  admits a formal expansion in powers of  $\tilde{n}(\mathbf{r})$ :

$$G[n] = G[n_0] + \int K(|\mathbf{r} - \mathbf{r}'|) \tilde{n}(\mathbf{r}) \tilde{n}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots \quad (21)$$

$K(|\mathbf{r} - \mathbf{r}'|)$  is a linear response function for the uniform and interacting electron gas which had been studied intensely by experts in many-body theory (Pines 1963). In particular, the derivative of its Fourier transform  $\tilde{K}(q)$  was known to diverge at a certain value of  $q$ . Walter knew this divergence well: it was responsible for the oscillatory algebraic form of the Friedel density disturbance formula in Eq. (6). It was also responsible for the “Kohn anomalies” in the phonon spectrum of metals. HK point this out and remark in passing that “the density oscillations in atoms which correspond to shell structure...are of the same general origin”.

<sup>99</sup> It is curious that Hohenberg and Kohn do not refer to papers by Hubbard (1958), Bellemans and Leener (1961), and Jones et al. (1962), all of whom studied the energy of an electron gas in the presence of a lattice of positive charges using methods superior to the Thomas–Fermi approximation.

The divergence in  $\tilde{K}(q)$  disappears if one retains only a finite number of terms in its power series expansion. The corresponding expansion of  $K(|\mathbf{r} - \mathbf{r}'|)$  reduces Eq. (21) to a *gradient expansion*,

$$G[n] = G[n_0] + a \int \tilde{n}(\mathbf{r}) d\mathbf{r} + b \int |\nabla \tilde{n}(\mathbf{r})|^2 d\mathbf{r} + \dots, \quad (22)$$

where  $a$  and  $b$  are constants related to  $\tilde{K}(q)$ . Therefore, as HK pointed out, any “quantum oscillations” produced by the divergence in  $\tilde{K}(q)$  cannot be captured by any low-order gradient expansion of  $G[n]$  like Eq. (22). This explained the failures of the many generalizations of the Thomas–Fermi approximation which involved adding gradient terms.

Finally, Hohenberg and Kohn focused on  $G[n]$  for a system with a slowly varying density function. This assumption precluded variations with short (spatial) wavelengths, but allowed for the possibility of substantial variations in the overall magnitude of the density. For this case, the appropriate gradient-type expansion is

$$G[n] = \int g_0(n(\mathbf{r})) d\mathbf{r} + \int g_2(n(\mathbf{r})) |\nabla n(\mathbf{r})|^2 d\mathbf{r} + \dots, \quad (23)$$

where  $g_0$  and  $g_2$  are functions (not functionals) of  $n(\mathbf{r})$ . By specializing Eq. (23) to the previously studied case of a nearly uniform electron gas, HK were able to express these functions in terms of the properties of the uniform and interacting electron gas. For example,  $g_0(n)$  is the sum of the kinetic energy density, the exchange energy density, and the correlation energy density for an interacting electron gas with uniform density  $n$ . With this information, HK performed a partial (infinite) summation of the entire gradient expansion in Eq. (23). Their final expression had the great virtue of recovering the singularity in  $\tilde{K}(q)$  needed to describe quantum oscillations.

Kohn left Paris in January 1964 and visited physicists in London, Cambridge, and Oxford before returning to California. He wrote up a first draft of a manuscript and sent it to Hohenberg for his review. Pierre made several suggestions, all of which were incorporated into the final version. The paper was sent off to the *Physical Review* in the second week of June 1964 and published in the November 9 issue. It is notable that the Concluding Remarks section does not remind the reader of the two theorems proved at the beginning of the paper. Instead, the authors remark that they “have developed a theory of the electronic ground state which is exact in two limiting cases”. The importance Hohenberg and Kohn ascribed to the ability of their theory to capture quantum oscillations may be judged from the fact that their paper ends with the statement that “the most promising formulation of the theory...appears to be that obtained by partial summation of the gradient expansion”. They say this despite warning the reader in the previous sentence that “actual electronic systems” have neither nearly constant densities nor slowly varying densities, i.e., the situations where the partial summation was expected to be valid.

Any reader of Hohenberg and Kohn (1964) cannot help but be struck by its understated and rather formal tone. The introduction is succinct, the basic theorems are proved quickly, most of the paper is taken up with the gradient expansions, and no

applications are discussed or proposed. Earlier, I quoted Kohn to the effect that he understood that the basic theorem which drives the paper was “remarkable”. If so, he and Hohenberg made a conscious decision not to emphasize the truly revolutionary idea at its core: that the ground-state electron density, in principle, determines all the properties of an electronic system. That being said, we learn from their 1990 reminiscence that the authors spent at least a little time talking about applications (Hohenberg et al. 1990):

The question arose as to what the method might be good for, and Kohn suggested that one could try using it to improve current techniques for calculating the band structure of solids. Hohenberg’s immediate reaction was to say, “But band structure calculations are horribly complicated, isn’t that the sort of stuff better left to professionals?” To this, Kohn simply replied, “Young man, I am the Kohn of Kohn and Rostoker (1954)!”

A recommendation from Kohn helped Hohenberg win a job at Bell Telephone laboratories in the fall of 1964. Recently, he recalled that “I gave a talk on my Paris work during my first few months at Bell Labs. Phil Anderson, Bill McMillan, and Phil Platzman were in the audience, and there was no enthusiasm. They correctly understood that our results would not help them solve the difficult many-body problems they were struggling with” (PH12). In the event, Hohenberg turned to hydrodynamics and phase transitions as topics for research and worked productively in those areas over a 30-year career at Bell. He was elected to the US National Academy of Sciences in 1989 and moved to Yale University in 1995 to accept the position of Deputy Provost for Science and Technology. Since 2004, he has served at New York University as a professor of physics and Vice Provost for Research.

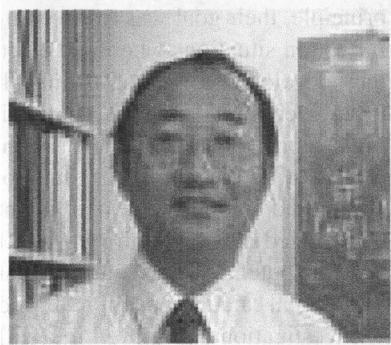
## 6 The work of Kohn and Sham

Kohn returned to La Jolla in early 1964 “to find a group of postdocs and visitors eagerly awaiting a first-hand account of the work” (Hohenberg et al. 1990). According to one of those postdocs, Vittorio Celli (VC13),

Walter gave a full departmental colloquium rather than just a technical seminar after his return from Paris. Keith Brueckner (who had returned from Washington and was Dean at the time) said that colloquia were usually reserved for “foreign stars” but that today we have “our own star” to give a talk. I remember thinking that the theory with Hohenberg was cute but would not have many consequences. I certainly did not think it compared in significance with the many-body calculations for the electron gas that had been obtained by Brueckner and his collaborators.

Kohn proposed to another postdoc, N. David Mermin, that he exploit his knowledge of statistical mechanics to generalize the Hohenberg–Kohn results to nonzero temperature. Mermin realized almost immediately that “a strange variational principle for the free energy that I had formulated for an utterly unrelated purpose” was perfectly suited for the job. As a result, “it took me less than an hour to check that the HK proof

**Fig. 11** Lu Jeu Sham (circa early 1980s) was a postdoc with Walter Kohn from 1963 to 1966.  
Courtesy of Lu Jeu Sham



went through” almost without change (Mermin 2003). Kohn was skeptical, but the simplicity of the proof could not be assailed. On the other hand, the significance of Mermin’s work was not very clear and he was disinclined to write it up. It took six months, his imminent departure from La Jolla, and Kohn’s insistence that “it someday might be important” for the manuscript of Mermin (1965) to get written (DM13).

Kohn’s colloquium featuring the Hohenberg–Kohn theorems generated skepticism from several of the many-body theorists who were in La Jolla to work with Keith Brueckner. Most notably, “Nobuyuki Fukuda, visiting from the University of Tokyo, constructed counter example after counter-example purporting to demonstrate the non-uniqueness of the potential given a density distribution. The job of resolving these fell to Lu Jeu Sham” (Hohenberg et al. 1990) (Fig. 11).

Lu Sham was the graduating Ph.D. student to whom Kohn had written requesting that he begin his postdoctoral fellowship at UCSD while Kohn was still in Paris. Sham, a native of Hong Kong, arrived in San Diego by way of Imperial College and Cambridge University where he had earned, respectively, an undergraduate degree in mathematics and a graduate degree in physics. His 1963 Ph.D. thesis, “The electron-phonon interaction,” was supervised by John Ziman, a distinguished theorist whose books, *Electrons and Phonons* (1960) and *Principles of the Theory of Solids* (1964), helped train a generation of solid-state physicists. In La Jolla, Sham used the months before Kohn returned to write a paper on the phonon spectrum of sodium metal. This quantitative calculation used a pseudo-potential for the sodium ionic potential and a self-consistent modification of the Hartree–Fock method to take approximate account of correlation effects which act to screen (reduce) the exchange interaction (Sham 1965).

Quantum density oscillations were much on Walter’s mind when he related the details of his Paris experience to Sham. He was acutely aware that no oscillations would emerge from Eq. (22), the most natural choice for  $G[n]$  when the external potential was a slowly varying function of position. Therefore, in the same letter where Walter informed Pierre Hohenberg that the HK manuscript had been submitted for publication, he related that “Lu Sham and I have started looking at situations like a heavy atom where one has a localized and rapidly varying potential”.<sup>100</sup> In

<sup>100</sup> WKP. June 15, 1964, letter from Walter Kohn to Pierre Hohenberg.

principle, their goal was to develop a general theory of quantum density oscillations for use in situations where the electron density is strongly non-uniform. In practice, they developed a method to find the leading quantum corrections to the Thomas–Fermi electron density for a collection of non-interacting electrons moving in a one-dimensional potential. The published paper, Kohn and Sham (1965a), reports the results of an elegant Green function calculation which related the electron density (which did exhibit the desired quantum oscillations) to the potential in a way which generalized Eq. (13). Unfortunately, the extension of their method to three-dimensional periodic potentials presented a daunting numerical challenge which did not lend itself to practical calculations for real solids. Accordingly, Kohn and Sham dropped this line of investigation and moved in a different direction, albeit one still motivated by the basic results obtained by Hohenberg and Kohn.<sup>101</sup>

By the late fall of 1964, Kohn was thinking about alternative ways to transform the theory he and Hohenberg had developed into a practical scheme for atomic, molecular, and solid-state calculations. Happily, he was very well acquainted with an approximate approach to the many-electron problem that was notably superior to the Thomas–Fermi method, at least for the case of atoms. This was a theory proposed by Douglas Hartree in 1928 which exploited the then just-published Schrödinger equation in a heuristic way to calculate the orbital wave functions  $\phi_k(\mathbf{r})$ , the electron binding energies  $\epsilon_k$ , and the charge density  $n(\mathbf{r})$  of an  $N$ -electron atom (Park 2009; Zangwill 2013). Hartree's theory transcended Thomas–Fermi theory primarily by its use of the exact quantum-mechanical expression for the kinetic energy of independent electrons. The *Hartree equations* which define the theory for an atom with nuclear charge  $Z = N$  are

$$-\frac{\hbar^2}{2m}\nabla^2\phi_k + [v_{\text{eff}}(\mathbf{r}) - \epsilon_k]\phi_k(\mathbf{r}) = 0, \quad k = 1, \dots, N, \quad (24)$$

where

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (25)$$

and  $v(\mathbf{r}) = -Ze^2/r$ . The electron density  $n(\mathbf{r})$  in Eq. (25) is calculated assuming that the electrons occupy that  $N$  lowest energy eigenfunctions of the Schrödinger equation in Eq. (24). Therefore, if  $k = 1, 2, \dots, N$  labels these  $N$  lowest energy orbitals,

$$n(\mathbf{r}) = \sum_{k=1}^N |\phi_k(\mathbf{r})|^2. \quad (26)$$

The effective potential energy function in Eq. (25) shows that every electron interacts with the charge of the “external” nucleus and with the charge of the entire atomic

<sup>101</sup> The Web of Science database (Accessed January 2014) lists 230 citations to the quantum density oscillations paper, Kohn and Sham (1965a). A review of these citations shows that the vast majority of the citing papers (>90 %) seem unaware of its actual content. They incorrectly cite it along with Hohenberg and Kohn (1964) and Kohn and Sham (1965b) as one of the foundational papers of density functional theory.

electron cloud taken as a whole.<sup>102</sup> Hartree stressed that these equations must be solved *self-consistently*. That is, an iterative numerical method is required to ensure that the  $\phi_k(\mathbf{r})$  generated by Eq. (24) are the same as the  $\phi_k(\mathbf{r})$  used in Eq. (26) to construct the particle density  $n(\mathbf{r})$ .

Slater (1930) and Fock (1930) provided a rigorous derivation of the Hartree equations. They used the variational principle in Eq. (1) and evaluated the total energy using a many-electron wave function of the form  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \cdots \phi_N(\mathbf{r}_N)$ . Minimizing this energy with respect to different choices for the  $\phi_k$  functions generates the Hartree equations. Slater and Fock also evaluated the total energy using a more sophisticated many-body wave function (today called a Slater determinant) which combines the same  $N$  orbital functions  $\phi_k$  in such a way that the Pauli exclusion principle is obeyed automatically. With this choice, minimizing the total energy with respect to choices for the  $\phi_k$  functions generates what are called the Hartree–Fock equations. Hartree–Fock theory is superior to Hartree theory because the kinetic energy *and* the exchange energy are treated exactly. Unfortunately, the Hartree–Fock equations are significantly harder to solve than the Hartree equations.

Kohn suggested to Sham that he try to derive the Hartree equations from the Hohenberg–Kohn formalism. Walter had good reason to believe this could be done (WK01, WK12). On the one hand, his work with Hohenberg had established the central role of the electron density  $n(\mathbf{r})$  for a complete description of any electronic system. On the other hand, the Hartree equations could be read as a self-consistent scheme to deduce an approximate expression for  $n(\mathbf{r})$ . Therefore, it should be possible to derive the Hartree equations as an *example* of the HK variational principle. Specifically, the variational minimization of some approximate form of the total energy functional  $E[n]$  should lead to Hartree's equations. Sham set to work with enthusiasm.

Kohn and Sham recognized that the Hartree method regards each electron as moving independently in an effective potential  $v_{\text{eff}}(\mathbf{r})$  which does not recognize the individual identity of the other electrons. Consistent with this, the kinetic energy implied by Eq. (24) is correct only for independent and non-interacting electrons. This was the key to progress because the Hohenberg–Kohn analysis implied that the kinetic energy of a strictly non-interacting system of electrons is also a functional of the density. If we call this functional  $T_S[n]$ , ordinary quantum mechanics specifies that<sup>103</sup>

$$T_S[n] = \sum_{k=1}^N \int \phi_k^*(\mathbf{r}) \left[ -\frac{\hbar^2}{2m} \nabla^2 \right] \phi_k(\mathbf{r}) d\mathbf{r}. \quad (27)$$

<sup>102</sup> In the actual equations written by Hartree (1928), each electron feels the classical electrostatic potential produced by every electron except itself. Therefore, in contrast to Eq. (25), each electron in Hartree's theory feels a slightly different electrostatic potential.

<sup>103</sup> The correctness of Eq. (27) requires that the functions  $\phi_i$  and  $\phi_j$  be orthonormal, which means that the integral  $\int \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r}$  is one when  $i = j$  and zero when  $i \neq j$ .

The path was now open for Sham to derive the Hartree equations from a density functional point of view. He chose the approximate total energy functional

$$E_H[n] = T_S[n] + \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + \frac{e^2}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (28)$$

and minimized it with respect to a density assumed to have the form in Eq. (26). The latter transforms the density variation of the first term in Eq. (28) into variations with respect to the  $\phi_k$  functions. The density variation of the remaining terms in Eq. (28) is straightforward, and the final result is exactly the Hartree equations (24) and (25).

Kohn and Sham (KS) now knew how to move forward with the general many-electron problem. Motivated by Eq. (28), they *defined* a functional  $E_{xc}[n]$  by the partition  $G[n] = T_S[n] + E_{xc}[n]$ . This puts the exact total energy functional in the form

$$E[n] = E_H[n] + E_{xc}[n]. \quad (29)$$

The great virtue of Eq. (29) is that it has exactly the same structure as Eq. (28), even if we revert to Eq. (7) for  $v(\mathbf{r})$ . Therefore, the interacting electron density  $n(\mathbf{r})$  which minimizes the original total energy in Eq. (10) is precisely equal to the non-interacting electron density  $n(\mathbf{r})$  which minimizes Eq. (29). Carrying out the latter minimization explicitly produces the *Kohn–Sham equations*, which are identical to the Hartree equations Eqs. (24) and (26) with Eq. (25) replaced by

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}) \quad (30)$$

where

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (31)$$

The exchange-correlation potential energy,  $v_{xc}(\mathbf{r})$ , obtained in Eq. (31) from the functional derivative of  $E_{xc}[n]$ , is a function of  $\mathbf{r}$  and not a functional of  $n(\mathbf{r})$ . Therefore, according to KS, a numerical procedure no more difficult than Hartree's original method is sufficient to compute the ground-state electron density and thus the ground-state total energy of an arbitrary many-electron system subject to an external potential. If  $E_{xc}[n]$  was known exactly, one could calculate  $n(\mathbf{r})$  and  $E[n]$  exactly as well.

The “exchange-correlation” energy functional  $E_{xc}[n]$  in Eq. (29) is similar to  $G[n]$  in Eq. (19) in the sense that it accounts for all the energy associated with the Coulomb interaction between electrons *not* already counted by the classical Coulomb self-energy. However, while  $G[n]$  had also to account for the total kinetic energy of the real interacting electron system [called  $T[n]$  in Eq. (16)],  $E_{xc}[n]$  has only to account for the *difference* between the kinetic energy of an interacting electron system and the kinetic energy of a non-interacting electron system with exactly the same density  $n(\mathbf{r})$ . Of course, the exact and universal functional  $E_{xc}[n]$  is no better known than  $G[n]$  for the interacting electron problem.

Unlike the Hartree–Fock theory sketched earlier, the foregoing derivation of the Hartree-like Kohn–Sham equations *does not introduce a many-electron wave function*

at any stage. Instead, Kohn and Sham replace the true interacting electron system with a non-interacting electron reference system which has exactly the same ground-state electron density. The wave function of the reference system is unambiguously Hartree-like, so it is correct to use the exact kinetic energy for non-interacting electrons in Eq. (27) and represent the density function as in Eq. (26). On the other hand, the eigenfunctions  $\phi_k(\mathbf{r})$  and the eigenvalues  $\epsilon_k$  in Eq. (24) have no direct physical meaning for the true interacting electron system.

Finally, Kohn and Sham proposed an approximation for  $E_{xc}[n]$  which has come to be known as the *local density approximation* (LDA). Namely,

$$E_{xc}[n] = \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) d\mathbf{r}, \quad (32)$$

where  $\epsilon_{xc}(n)$  is the exchange and correlation energy per electron of a fully interacting electron gas with uniform density  $n$ . Hohenberg and Kohn had introduced a similar approximation for  $G[n]$  in their paper, and it was reasonable for Kohn and Sham to “regard  $\epsilon_{xc}(n)$  as known from theories of the homogeneous electron gas”.<sup>104</sup> When Eq. (32) is used for  $E_{xc}[n]$ , the exchange-correlation potential in Eq. (31) becomes

$$v_{xc}(\mathbf{r}) = \frac{d}{dn} [n\epsilon_{xc}(n)]. \quad (33)$$

The foregoing results were reported in a short manuscript, “Exchange and correlation effects in an inhomogeneous gas” which Kohn and Sham submitted to *Physical Review Letters* in May of 1965. Samuel Goudsmit, one of the editors of *Physical Review Letters* at that time, informed Sham by letter that the Kohn–Sham manuscript “deserves publication as an Article in the *Physical Review*, but it is not of such urgency to warrant speedy publication in *Physical Review Letters*” (SG65). The authors responded by withdrawing the manuscript and, 3 weeks later, submitted to the *Physical Review* a longer and more detailed paper with a new title, “Self-consistent equations including exchange and correlation effects”. The published version, Kohn and Sham (1965b) is the second foundational paper of density functional theory. It is also one of the most highly cited papers in the history of physics.<sup>105</sup> Interestingly, it was only at the page-proof stage of the longer paper that the authors realized that their Hartree-like equations with Eq. (31) represented a formally exact statement of the complete many-body problem (LS14). For that reason, Eq. (31) appears only in a “Note Added in Proof” while Eq. (33) appears in the main exposition.

Kohn and Sham knew it was straightforward to use Eq. (33) to write down an explicit and analytic formula for  $v_{xc}(\mathbf{r})$  and incorporate it seamlessly into existing computer programs to calculate the electronic structure of atoms, molecules, and solids. Briefly, the separation  $\epsilon_{xc}(n) = \epsilon_x(n) + \epsilon_c(n)$  known for the interacting and

<sup>104</sup> The local density approximation for  $G[n]$  retains only the first term on the right-hand side of Eq. (23).

<sup>105</sup> The Web of Science database (accessed January 2014) lists 21,372 citations to Kohn and Sham (1965b). Only four physics-related papers have more citations, and all four of them are density functional papers which owe their existence to the Kohn–Sham paper. See also the bibliometric studies of Redner (2005) and Marx (2007).

uniform electron gas implies that the exchange-correlation potential Eq. (33) separates similarly into  $v_{xc}(\mathbf{r}) = v_x(\mathbf{r}) + v_c(\mathbf{r})$ . The exact exchange energy density,  $\epsilon_x(n)$ , had been calculated years earlier by Dirac (1930) for the purpose of improving the Thomas–Fermi approximation. Using Dirac’s formula, KS reported their result for the LDA exchange potential:<sup>106</sup>

$$v_{x,\text{LDA}}(\mathbf{r}) = -e^2 \left[ \frac{3}{\pi} n(\mathbf{r}) \right]^{1/3}. \quad (34)$$

This expression was consequential at the time because, when Eq. (34) replaces  $v_{xc}(\mathbf{r})$  in Eq. (30), the Kohn–Sham equations become almost identical to a set of equations John Slater had proposed in 1951 as a local approximation to the non-local Hartree–Fock equations. I say “almost” identical because the *ad hoc* local exchange potential proposed by Slater (1951) was

$$v_{x,\text{Slater}}(\mathbf{r}) = -\frac{3}{2} e^2 \left[ \frac{3}{\pi} n(\mathbf{r}) \right]^{1/3}. \quad (35)$$

KS argue for the correctness of their proposed exchange potential, and it is notable that the abstract of Kohn and Sham (1965b) devotes a sentence to announcing the factor of 3/2 difference between Eqs. (34) and (35). The authors’ motivation to do this was surely their awareness that the so-called “Hartree–Fock–Slater” method was in wide use by physicists performing band-structure calculations for real solids (Callaway 1958; Herman 1964).

The Kohn–Sham equations [with and without the local density approximation for  $v_{xc}(\mathbf{r})$ ] are the reason for the enduring importance of Kohn and Sham (1965b). The paper itself differs in tone from Hohenberg and Kohn (1964) in the sense that the abstract notion of an “inhomogeneous electron gas” disappears from the title and from most of the text. Instead, there is the practical promise of “self-consistent equations” appropriate to “real systems (atoms, molecules, solids, etc.) [where] the electronic density is non-uniform”. The introduction is even more specific and makes the point that

most theoretical many-body studies have been concerned with elementary excitations and as a result there has been little progress in the theory of cohesive energies, elastic constants, etc. of real metals and alloys. The methods proposed here offer the hope of new progress in the latter area.

That being said, KS did not themselves report any calculations of the cohesive energy or elastic constants (or any other measurable quantity) for any “real” electronic system. Indeed, they did not even bother to write down an explicit form for the correlation part of  $v_{xc}(\mathbf{r})$  in the local density approximation. This was a straightforward exercise for anyone familiar with the electron gas literature. As for the LDA itself, KS remark that it should “give a good representation of exchange and correlation effects...for

<sup>106</sup> Kohn and Sham were unaware that the Hungarian physicist Rezső Gáspár had derived Eq. (34) 10 years earlier by similarly computing the variational derivative of Dirac’s exchange energy with a local density approximation (Gáspár 1954).

metals, alloys, and small-gap insulators". On the other hand, they warn the reader that the LDA should have "no validity [at] the 'surface' of atoms and the overlap regions of molecules... We do not expect an accurate description of chemical binding".

Walter left for his annual visit to Bell Labs after the June 1965 submission of the longer Kohn–Sham manuscript. He collaborated with Quin Luttinger as usual and their efforts produced a prediction for a new mechanism for superconductivity based on a presumed oscillatory interaction between pairs of electrons (Kohn and Luttinger 1965). Meanwhile, back in La Jolla, Lu Sham began work on two density functional projects. One of these, which became the final paper he and Kohn would publish together, examined the one-body Green function of many-body theory (Sham and Kohn 1966). It was important for them to study this quantity because its properties determine the energy, lifetime, and spatial extent of single-particle-like excitations out of the ground state of a many-body system. At the same time, the Hohenberg–Kohn theory implies that the Green function itself is as a functional of the ground-state electron density.

Sham, who did most of the calculations, demanded that the Green function satisfy the requirements of particle-number conservation and charge neutrality and deduced thereby that an electron at a point  $\mathbf{r}$  in an atom, molecule, or solid responds to the electrostatic potential at that point and to exchange and correlation effects which depend on the electron density distribution in the immediate vicinity of  $\mathbf{r}$  only. For a slowly varying density, this conclusion justifies a local density approximation for the Green function, which in turn provides an approximation for the energy spectrum and an independent justification for using the LDA with the Kohn–Sham equations to calculate the ground-state electron density  $n(\mathbf{r})$ .

Sham's second post-Kohn–Sham density functional project was done in collaboration with Bok Yin (Philip) Tong, a 30-year-old graduate student who had begun to work with Kohn. Their goal was to solve the Kohn–Sham equations numerically for several atoms and ions. Luckily for them, Frank Herman and Sherwood Skillman had just published a computer program which solved the Hartee–Fock–Slater equations for atoms (Herman and Skillman 1963). Tong and Sham needed only to replace Eq. (35) by Eq. (34) in the program and add some code for the correlation part of  $v_{xc}(\mathbf{r})$  in the LDA. For this, they used an interpolation formula for the correlation energy derived from the information given in Pines (1963). The published paper, Tong and Sham (1966), focused on total energies, total energy differences, and charge densities. The final results with correlation omitted were gratifying, giving "slightly better results for energies and substantially better results for densities than Slater's method". The correlation correction worsened the results, "presumably because the electronic density in atoms has too rapid a spatial variation".

Lu Sham published three articles unrelated to density functional theory before beginning an Assistant Professorship at the University of California at Irvine in the fall of 1966. Two years later, he accepted an offer to return to La Jolla as an Associate Professor. He was promoted to Professor in 1975, served as a Dean from 1985 to 1989, and is currently Emeritus Professor of Physics. He was elected to the US National Academy of Sciences in 1998. At UCSD, Sham developed a broad research program with a particular expertise in the theory of the electronic and optical properties of semiconductor heterostructures. However, the twenty papers he published on density

functional theory over the years show that he never completely abandoned the main subject of his postdoctoral work.

Walter Kohn remained at San Diego until 1979, when he accepted the position as founding Director of the Institute for Theoretical Physics (ITP), a research facility established and supported by the US National Science Foundation at the University of California at Santa Barbara. He served as Director for 5 years and continued as a Professor of Physics at UCSB until 1991 when he gained Emeritus status. Kohn and his collaborators published over 150 papers between 1965 and 2006. One-third of these explore some aspect of density functional theory, particularly its application to solid surfaces. An equal number of papers concern Kohn's pre-DFT interests including disordered states of matter, superconductivity, Bloch and Wannier functions, scattering theory, and the transition between the conducting and insulating states of matter. Kohn was elected to the National Academy of Sciences (1969) and was a recipient of a National Medal of Science (1998) before winning a share of the 1998 Nobel Prize in Chemistry.

## 7 Discussion and conclusion

In March 2001, Kohn addressed a symposium on "The History of the Electronic Structure of Atoms, Molecules, and Solids" at a meeting of the American Physical Society. With an audience well schooled to interpret the lower case Greek letter  $\epsilon$  as an infinitesimally small quantity, Walter was understood immediately when he characterized the initial reception of density functional theory as "+  $\epsilon$  by theoretical physicists and zero by theoretical chemists" (WK01). The meager reaction by physicists reflected the fact that Kohn's theory did not directly address the "big" issues that occupied many solid-state physicists at the time: superconductivity, the Kondo effect, superfluid helium, disorder-induced localization, the metal-insulator transition, and quasi-one-dimensional conductors. The positive response was limited mostly to band-structure theorists who were well positioned to carry out the numerical work needed to solve the Kohn-Sham equations for real materials.<sup>107</sup> The lack of response (or negative response) from chemists stemmed mostly from their near-universal belief that no theory of electronic structure based on the particle density alone could possibly be correct. In a future publication, I will trace the evolving response of both the physics and chemistry communities to DFT. For the present, it suffices to sketch very briefly the path which led from virtually no response by chemists to a Nobel Prize in Chemistry.

An important point mentioned earlier is that a computer program written to solve the local exchange potential equations of the Hartree-Fock-Slater (HFS) method (Slater 1951) was easily adapted to solve the Kohn-Sham equations in the local density approximation. Therefore, after the 1965 publication of the Kohn-Sham paper, systematic calculations for atoms began to reveal that Eq. (34) was superior to Eq. (35) as

<sup>107</sup> Despite the warning in Sham and Kohn (1966) that the  $\epsilon_k$  parameters should not be interpreted as one-electron energies, "the temptation to use [them] as band structures in solids proved irresistible" (Hohenberg et al. 1990).

a local approximation to the exact, non-local exchange potential (Herman et al. 1969). HFS and LDA calculations for molecules and solids were more difficult to evaluate because computational exigencies encouraged the use of a “muffin-tin approximation” where the effective potential in Eq. (30) was replaced by its spherical average inside a set of touching spheres centered at the atoms. A constant potential was used outside the spheres.

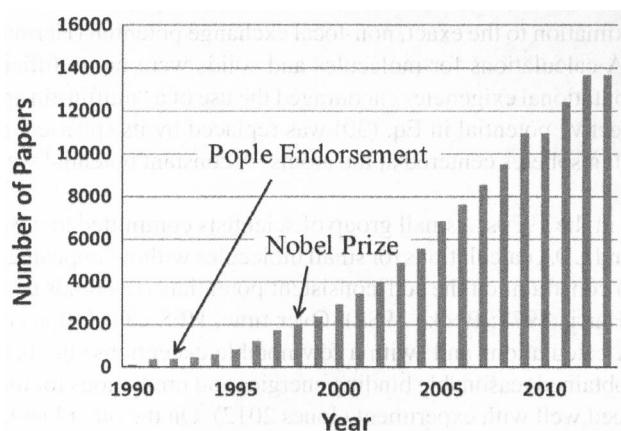
Beginning in the 1970s, a small group of scientists committed themselves to carrying out HFS and LDA calculations for small molecules without imposing the muffin-tin (or any other) constraint on the self-consistent potentials (Baerends et al. 1973; Gunnarsson and Harris 1977; Becke 1982). Over time, HFS calculations disappeared in favor of LDA calculations and (with a few notable exceptions) the basic conclusion was that one obtained reasonable binding energies and predictions for molecular structures that agreed well with experiment (Jones 2012). On the other hand, the LDA was *not* capable of the kind of “chemical accuracy” ( $\pm 2$  kcal/mole) that the best ab initio methods of traditional quantum chemistry could achieve. Then, in the 1980s, efforts to go beyond the local density approximation led to the proposal and testing of various non-local approximations for the exchange and correlation functional (Langreth and Mehl 1983; Perdew 1986; Becke 1988; Lee et al. 1988). These, so-called “generalized gradient approximations” (GGA) replaced the electron gas exchange-correlation energy density in Eq. (32) with much more complicated functions of both the local density  $n(\mathbf{r})$  and the local density gradient  $\nabla n(\mathbf{r})$ .<sup>108</sup> Systematic Kohn–Sham calculations for atoms and molecules using GGA, particularly a hybrid approach introduced by Becke (1993), quickly began to approach chemical accuracy.

A turning point occurred in 1991 at the VIIth International Congress of Quantum Chemistry in Menton, France (WK13b). John Pople gave the final talk and summarized the achievements of “G2” theory, his most comprehensive ab initio attempt to improve the Hartree–Fock approximation using perturbation theory (Curtiss et al. 1991). On the other hand, earlier in the week, the Congress had given its triennial “outstanding young scientist” award to Axel Becke for his manifestly non-ab-initio work with DFT. Specifically, “for unique advances in numerical methods in density functional theory as applied to molecules, and for important developments in the understanding of the exchange-correlation functional that enters density functional theory”.<sup>109</sup> Pople made a point in his talk to remark that he found Becke’s results “stimulating and intriguing” (JP91).

Barely a year later, Pople’s group published a systematic comparison of the best quantum chemical calculations with DFT calculations performed using a variety of exchange-correlation potentials for 32 molecules. They concluded that the most sophisticated non-local functionals “outperformed correlated ab initio methods, which are computationally more expensive. Good agreement with experiment was obtained with a small basis set” (Johnson et al. 1992). DFT was promptly incorporated into Pople’s widely used GAUSSIAN computer program, and, with this endorsement, the popularity of DFT calculations among chemists began to grow exponentially (see

<sup>108</sup> The generalized gradient approximations go far beyond the simple gradient expansions analyzed by HK and KS.

<sup>109</sup> Awards of the IAQMS.



**Fig. 12** Numbers of papers that mention DFT as found by the Web of Science

Fig. 12 and Ref.<sup>110</sup>). Accordingly, when the Nobel Chemistry Committee decided it was time to honor quantum chemistry with a Prize, it was not difficult for them to split the award between John Pople and Walter Kohn.

At the beginning of this paper, I suggested that density functional theory might be unknown today if Walter Kohn had not created it in the mid-1960s. Such a counterfactual claim can never be proved. However, it is interesting to examine the evidence that supports it. We do this with full awareness of a long tradition which examines great scientific discoveries from the *personalistic* and *naturalistic* points of view (Boring 1950). The former focuses on the specific attributes of an individual whose “exceptional insight may lead to an original discovery which has not been anticipated by others and which is relatively independent of the times”. The latter posits that “the *zeitgeist* (scientific climate of the time) determines the great discovery and that he who makes the discovery is great merely because the times employed him”. Here, I begin with the *zeitgeist* of electronic structure theory in Kohn’s lifetime and then turn to his particularism for the case of DFT.

The modern concept of the electronic structure of atoms, molecules, and solids began when the old quantum theory of Bohr gave way to the new quantum theory of Schrödinger (Jammer 1966). From 1925 to 1960, at least 1,000 papers in the scientific literature concerned themselves with the “many-electron” problem.<sup>111</sup> One thousand more papers focused on this topic between 1961 and 1965. The abstracts of these papers reveal five principal approaches to this issue: the Thomas–Fermi method, electron gas models, many-electron wave function methods, density matrix methods, and quantum field theory methods. Of these, only the approximate Thomas–Fermi method singles out the ground-state electron density  $n(\mathbf{r})$  as the primary quantity for study. Attempts to build “quantum corrections” into the Thomas–Fermi model were current in the early 1960s, but none suggested that the theory could be “exactified” to reveal the

<sup>110</sup> Redner (2005) and Marx (2007) are two bibliometric studies which discuss DFT.

<sup>111</sup> Data collected from Google Scholar in January 2014. The true number of papers is higher because not all authors used the term “many-electron” in their writing.

density as a truly fundamental quantity. A paper inspired by Friedel's alloy work, which ignores correlation and derives a formal perturbation series for the density in term of the external potential, is perhaps closest in this regard (March and Murray 1961).

In the late 1950s and early 1960s, the ground-state electron density was not very interesting to many theoretical solid-state physicists. They focused instead on the excited states of solids and the powerful new methods of quantum field theory which made their study possible (Hoddeson et al. 1992). Those who did appreciate the general importance of the charge density—primarily the practitioners of band-structure calculations—saw no reason and had no motivation to elevate it to the lofty status of the many-electron wave function (Herman 1958; Pincherle 1960). The latter attitude was shared by the quantum chemistry community who devoted enormous efforts to solving the Schrödinger equation for molecules with greater and greater accuracy (Barden and Schaeffer 2000; Gavroglu and Simões 2012). An interesting exception is the Canadian Richard Bader, perhaps the greatest champion of  $n(\mathbf{r})$  among theoretical chemists. Just a year before the publication of Hohenberg and Kohn (1964), he wrote (Bader and Jones 1963):

The manner in which the electron density is disposed in a molecule has not received the attention its importance would seem to merit. Unlike the energy of a molecular system, which requires a knowledge of the second-order density matrix for its evaluation, many of the observable properties of a molecule are determined in whole or in part by the simple three-dimensional electron density distribution.

Despite his fondness for the density, even Bader could not deny the primacy of the second-order density matrix (Löwdin 1959). This was the rock-solid quantum chemical view that Hohenberg had discovered in Paris when he reviewed the literature of many-electron theory.

To my knowledge, the only work in the pre-1964 electronic structure literature where the electron density plays a fundamental role is a one-page paper by the distinguished theoretical chemist, Wilson (1962). Wilson asks the rhetorical question, "Does there exist some procedure for calculating  $n(\mathbf{r})$  [for an  $N$ -electron system] which avoids altogether the use of  $3N$  dimensional space?" He then uses a device mentioned earlier (see Sect. 4) and defines  $n(\mathbf{r}, \lambda)$  to be the exact ground-state electron density of a many-electron system where the charge of every electron is taken to be  $\lambda e$  rather than  $e$ . Using just a few lines of calculation, Wilson shows that the total energy  $E$  in Eq. (10) can be written as an integral from  $\lambda = 0$  to  $\lambda = 1$  of the sum of the classical Coulomb potentials produced by  $n(\mathbf{r}, \lambda)$  at the positions of all the nuclei.<sup>112</sup>

From the foregoing, I conclude that no scientists before Walter Kohn in 1963 were even vaguely thinking about using the ground-state charge density as a fundamental

<sup>112</sup> According to Musher (1966), Wilson's method goes back to Pauli.

quantity from which to build an exact theory of a many-electron system.<sup>113</sup> The idea was not “in the air,” and all eyes were riveted either on the many-electron wave function, the first- and second-order density matrices, or the Green functions of many-body field theory. The zeitgeist of electronic structure theory was simply not moving in the direction of the electron density function for some particular well-prepared scientist to exploit and earn the accolades of discovery.

I now turn to Kohn himself. Section IV detailed how Walter chose to focus his fall 1963 sabbatical leave on a problem that was *not* under active investigation by many of his theoretical colleagues. Namely, how might one calculate the electronic structure of a three-dimensional disordered metal alloy, a system with no underlying spatial periodicity?<sup>114</sup> His study of the metallurgy and metal physics literature inspired him to ask whether the electron density  $n(\mathbf{r})$  was sufficient to completely characterize a many-electron system. It must be admitted that Kohn was a product of his scientific milieu as much as any other electronic structure theorist working at the time. Therefore, the mere fact that this question came to his mind *and he took it seriously* must be regarded as a legitimate “eureka moment” which few are privileged to experience. That being said, I wish to argue further that his particular history, style of research, and scientific tastes made him unusually well suited to exploit this insight and create from it the edifice of density functional theory.

Two aspects of Kohn’s pre-college years (surveyed in Sect. 2) bear on the narrow question of his future life as a physicist. First, the cataclysm of the *Anschluss* put the budding classics scholar into contact with Emil Nohel and Victor Sabbath, two high school teachers whose passion for their subjects converted him to an enthusiastic student of mathematics and physics. Second, the camp schools Kohn attended while interned in Canada exposed him to sophisticated one-on-one instruction from professional scientists. A pedagogical experience of this kind is barely imaginable at a conventional high school, then or now. In a normal setting, there is little chance that the teenaged Kohn would have encountered (much less devoured) books like Hardy’s *A Course in Pure Mathematics* and Slater’s *Introduction to Chemical Physics*.<sup>115</sup>

Walter’s undergraduate and master’s level classroom experiences at the University of Toronto were probably typical of first-rate academic institutions at the time. What

<sup>113</sup> Dirac (1930) states that “the whole state of the atom is completely described simply by this electric density; it is not necessary to specify the individual three-dimensional wave functions that make up the total electric density”. However, it is clear from context that the word “density” is used here to mean the quantum mechanical density matrix. In the last section of the paper, Dirac identifies the approximations required to reduce his density matrix description to a classical scalar density description. The result is a generalization of the Thomas–Fermi approximation.

<sup>114</sup> Early work on this problem published by Korringa (1958) and Beeby (1964) blossomed into a full-scale theory of the electronic structure of disordered alloys in the late 1960s and early 1970s (Ehrenreich and Schwartz 1976).

<sup>115</sup> It is impossible to know how the frightful loss of his home and parents to Nazi terror motivated Kohn to succeed in later life. A statistical study of Viennese children who had similar experiences during World War II and then emigrated to America shows that those who entered the sciences achieved success (by conventional measures) more than twice as often as native-born American scientists of the same generation. The study quotes several participants who said “they felt a great responsibility to make the most of their lives because their survival was such a rare and unlikely event”. (Sonnert and Holton 2006).

was not typical was the unusually high caliber of the individuals who mentored him and who (because of their own professional interests) repeatedly emphasized variational principles for both general proofs and for detailed numerical calculations. It is true that all well-trained theoretical physicists learn about variational principles and many use them occasionally in their professional work. However, very few physicists who learn about them as undergraduates go on to work with a doctoral supervisor like Julian Schwinger who attacked almost every problem from a variational point of view, and then write a thesis where variational principles are used (again) both to prove a general result and to obtain numerical results for a specific quantum situation. Fundamental and numerical variational calculations appear over and over again in Kohn's solid-state work at Carnegie Tech and Bell Labs through the 1950s. It is little wonder that he turned quickly to this powerful tool when he sought to prove the first Hohenberg–Kohn theorem, which states that the many-body wave function and everything calculable from it are functionals of the ground-state electron density  $n(\mathbf{r})$ . The second Hohenberg–Kohn theorem, which states that the total energy takes its minimum value when  $n(\mathbf{r})$  is the exact ground-state density, is explicitly a variational result.

The Hohenberg–Kohn paper is austere, elegant, and deep. Like several other papers in his oeuvre, it demonstrates a characteristic of his work that a Kohn-watcher of 50 years tenure summarized in this way (Langer 2003):

He always has loved mathematical elegance, but he reserves it for situations where it is truly necessary. His emphasis [is always] on the most important physical questions and the ways in which they could be answered with insight and confidence.

This observation is interesting and important, but it does not distinguish Kohn from a number of other theoretical physicists with a taste for proving theorems. However, I believe it is unlikely that any of them would have had either the interest or the inclination to derive the Kohn–Sham equations and suggest the local density approximation for practical calculations. To make this case, I have surveyed the publications of the most active theoretical solid-state physicists working between 1950 and 1980. As a matter of personal taste, three broad activities engage them: formal calculations and proofs of theorems, analyses of model Hamiltonians, and numerical calculations for specific materials systems. If an individual was active in more than one of these, it was most often the first and second activities or the second and third activities. Kohn is unusual among his peers simply because he followed up a paper which asks and answers a deep theoretical question with a paper which constructs a practical tool to perform calculations for specific systems.

Kohn's own early research history demonstrates a willingness to compute actual numbers for direct comparison with experiment. The Kohn–Sham equations are the vehicle for this activity in the context of electronic structure theory. In practice, Kohn turned over much of the explicit numerical work on DFT to his students and postdocs, but there is complete agreement among this cohort that he never regarded this activity as a less important part of his group's research. This is the reason that a senior quantum chemist could remark that Kohn is “the least arrogant of the deep physicists” in the sense that he does not “give a lower standing to those parts of physics that deal



**Fig. 13** The physicist Walter Kohn learns a new trade after winning one-half the 1998 Nobel Prize in Chemistry. Drawing by Peter Meller. Courtesy of Walter Kohn

with the complexities of phenomena governed by known laws" (Baerends 2003). The "complexities" mentioned here are discovered only by carrying out numerical computations for specific systems using the "known laws" described by the Kohn-Sham formalism.

In summary, Walter Kohn earned one-half of the 1998 Nobel Prize in Chemistry by asking himself a simple (yet deep) scientific question about the electronic structure of matter. He answered that question in an elegant and thought-provoking manner and then exploited his result to re-formulate the quantum many-electron problem in a manner which made calculations for real systems computationally cheap and surprisingly accurate. These things may have been achieved by someone else if Kohn and his postdoctoral associates had not done so in the years 1963–1965, but that person would probably look very much like Walter Kohn himself (Fig. 13).

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## Appendix: Unpublished and archival sources

AA13 Anthony Arrott interview. July 19, 2103.

AG07 Griffin, A. Many-body physics in the 1960s: a golden age. A talk given at the symposium "50 years of Condensed Matter Physics". June 16, 2007. [http://www.lassp.cornell.edu/lassp\\_data/LASSP/50YearsCMP-VA2007.pdf](http://www.lassp.cornell.edu/lassp_data/LASSP/50YearsCMP-VA2007.pdf)

- AMP American Physical Society. <http://www.aps.org>
- AY13 Correspondence with Alice Carroll Young. May 2, 2013.
- CDW13 Program of the 1951 Summer School of Theoretical Physics, Les Houches, France. Courtesy of Prof. Cécile deWitt, University of Texas.
- CS13 Correspondence with C. Siochi, University of Toronto Alumni Relations Officer for the Faculty of Arts and Sciences. March 20, 2013.
- DM13 Correspondence with David Mermin. February 12, 2013.
- GF62 John Simon Guggenheim Memorial Foundation. Application letter of Walter Kohn. 1962. Used by permission of the Foundation and Walter Kohn.
- GFF46 Geoffroy, P.R. 1946. *Report on the Magnetometer Survey of the property of Dante Red Lake Gold Mines Ltd.* File 52N04N9958.pdf of the Ontario Ministry of Northern Development and Mines.
- GG13 Correspondence with G. Giannakis, McGill University Archives. August 6, 2013.
- HF13 Correspondence with Allen Horsley, Rose Shelton Horsley Cruz and Lucile Horsley Blanchard, children of Caperton B. Horsley, founder of the Sutton-Horsley Co. June 2013.
- IAQMS International Academy of Quantum Molecular Science. <http://www.iaqms.org>.
- JE13 Josef Eisinger interview. July 24, 2013.
- JF13 Correspondence with Jon Ford, Head Teacher, Imberhorne Secondary School, East Grinstead, England. June 19, 2013.
- JP91 Pople, J.A. 1991. The computation of molecular energies. Video recording of an invited talk to the VIIth International Congress of Quantum Chemistry. Courtesy of Prof. Axel Becke.
- KB85 Brueckner, K. 1985. Early Development of the UCLJ Physics Department. pp. 5–9 in: Proceedings of the La Jolla Physics Symposium, UCLJ 1960–1965. [http://physics.ucsd.edu/dept/department\\_history.pdf](http://physics.ucsd.edu/dept/department_history.pdf)
- KB94 Brueckner, K. 1994. First years at the University of California at San Diego, 1959 to 1965. [http://libraries.ucsd.edu/historyofucsd/#iw\\_bruecknerfirstyears](http://libraries.ucsd.edu/historyofucsd/#iw_bruecknerfirstyears)
- KH99 Hanta, K. 1999. From exile to excellence: an interview with Nobel prize laureate Walter Kohn. *Austria Kultur* 9 (1). <http://www.auslandsdienst.at/de/projekt/pressearchiv-1999/austria-kultur-vol-9-no1-januaryfebruary-1999-exile-excellence-interview>
- LB13 Correspondence with Louis W. Bruch. April 10 2013.
- LG13 Larry Glasser interview. August 6, 2013.
- LS14 Correspondence with Lu Jeu Sham. January 10 2014.
- MR13 Max Luming Ren interview. July 20, 2013.
- NBA Niels Bohr Archive. Copenhagen.
- NPC Nobel Prize in Chemistry 1998. [http://www.nobelprize.org/nobel\\_prizes/chemistry/laureates/1998](http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1998)
- NR13 Norman Rostoker interview. July 23, 2013.
- PA77 Philip Anderson Nobel Prize autobiography. [http://www.nobelprize.org/nobel\\_prizes/physics/laureates/1977/anderson-bio.html](http://www.nobelprize.org/nobel_prizes/physics/laureates/1977/anderson-bio.html)

- PA99 Philip W. Anderson interview conducted by Alexei Kojevnikov. May 29, 1999. Niels Bohr Library and Archives, College Park, MD.
- PF13 Peter J. Feibelman interview. June 28, 2013.
- PH12 Pierre Hohenberg interview. July 19, 2012.
- PN12 Correspondence with Philippe Nozières. July 6 2012.
- PRL64 Memorandum from the Editors of *Physical Review Letters*. October 1964.
- RF13 Robert Fletcher interview. October 30 2013.
- RS51 Silverman, R.A. 1951. *The Fermi Energy of Metallic Lithium*. Ph.D. thesis. Harvard University.
- SG65 Letter from S.A. Goudsmit to L.J. Sham. May 28 1965. Courtesy of Lu Jeu Sham.
- TK59 Kjeldaa, T. 1959. *Theory of Ultrasonic Cyclotron Resonance in Metals at Low Temperature*. Ph.D. Thesis. University of Pittsburgh.
- UCSDA University of California San Diego Archives. News Release. September 15 1960.
- VA13 Vinay Ambegaokar interview. May 12, 2013.
- VC13 Vittorio Celli interview. February 8, 2013.
- WK00a Walter Kohn interview conducted by N. Hollander. Nobel Voices Video History Project. 2000. Archives Center. Smithsonian National Museum of Natural History.
- WK00b Letter of August 23, 2000, from Walter Kohn to the Principal of the Imber-horne Secondary School, East Grinstead, England. Courtesy of Jon Ford.
- WK01 A personal account of the history of density functional theory. Session S3 (History of electronic structure theory in atoms, molecules, and solids), American Physical Society annual meeting, March 14, 2001, Seattle, WA. Sound recording AV 2001-374z used with the permission of the Niels Bohr Library and Archives, American Institute of Physics, College Park, MD 20740, USA.
- WK03 A fireside chat with Nobel Laureate Professor Walter Kohn. An August 15, 2003, broadcast by the University of California Television. <http://www.youtube.com/watch?v=VDNNiKdtyhg>.
- WK12 Walter Kohn interview. December 18, 2012.
- WK13a Walter Kohn interview conducted by Nina Krieger. March 3, 2013. Internment Project of the Vancouver Holocaust Education Centre.
- WK13b Walter Kohn interview. October 8, 2013.
- WK98 Walter Kohn Nobel Prize autobiography. [http://www.nobelprize.org/nobel\\_prizes/chemistry/laureates/1998/kohn-autobio.html](http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1998/kohn-autobio.html)
- WKP Walter Kohn Papers. University of California, Santa Barbara.

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