My Life in Science: Lessons for Yours?

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Abstract:

Because of an acquired obsession to understand as much as possible in a limited but important area of science, and because of optimism, luck and help from others, my life in science turned out to be much better than I or others could have expected or planned. This is the story of how that happened, and also the story of the ground-state density functional theory of electronic structure, told from a personal perspective.

What might be achieved by writing an autobiography?

When I write a research article, I usually start with science that I would like to understand better, and that I would like my readers to understand better. Writing focuses the mind, bringing clarity and preserving it for the future. In my 80 years of life, I have written over 360 research articles, almost entirely in the density functional theory of the electronic structure of matter.

The editors of this special issue of the Journal of Chemical Physics have asked me to write an autobiography – a new endeavor for me. What can I understand better about my own life, and how can I make that understanding interesting or useful to my readers (presumably scientists, including some at an early stage of their careers)? I think I should focus on the factors (personal traits, other people, experiences, accidents) that contributed to or limited whatever I have achieved in science, and only on those. No one else will have exactly the same factors, but all of us encounter positive and negative factors, and need to be able to put them in perspective. I should also focus on density functional theory and its history, not on all of it but on the parts that I personally know.

Within this scope, I will aim to be truthful, but we all know that memories can fade or simplify over time.

To keep this article at a readable length, some arbitrary decisions had to be made about what and whom to include or omit. Many excellent students, postdocs, senior collaborators, and friends are missing here (except perhaps in the Appendix, which lists most of my past and present research group members), but not in my memory. I have enjoyed and benefitted from knowing and working with many good, bright, and innovative people over the years.

Early years 1943-1961

My father was a high-school biology teacher, and my mother was an elementary school teacher. So I grew up in an environment in which science, mathematics, language, and education were important. My mother spent many years at home, nurturing and educating me, before she returned to school teaching. I knew letters, numbers, and arithmetic, and could read a little, before the first grade. I was told (but don't remember) that on my first day of school I gave a lecture about the solar system.

I remember radio, before television. Radio might have been a better preparation for science, because it left more to the imagination.

Public school was easy for me, but the courses I liked best and from which I benefited most in my career were English reading/writing and mathematics. I read widely: novels, plays, science, science fiction, philosophy, economics, and history, up to and including my undergraduate and graduate years, but after that I narrowed down and read mostly physics/chemistry. The reading that I did made me aware of the high level of style and clarity that can be achieved in good writing. My high school courses in geometry, trigonometry, algebra, and calculus were well taught, and opened my eyes to the possibility of proving or disproving assertions.

I was a high school student when the Russians launched their Sputnik satellite in 1957. The American rockets with Vanguard satellites kept exploding on the launch pad, and there was an American consensus to build up science and technology. Our school board in Maryland decided to offer a concentrated physics course to senior students, and to devote two hours per day to it. But they could not find anyone who knew physics to teach it. Eventually they hired a former basketball coach, who may have been overconfident about his ability to teach himself the subject. In his first daily hour, he delivered the same lecture about the relationship between density (!), mass, and volume, in its three permutations, and his second daily hour was a study hall. The only time I was ever sent to the principal's office for discipline was when I read a historical novel during the first hour of physics class. At the end of the semester, our teacher decided that he had overlooked two important subjects (the Bohr theory of the atom and Morse code), so he handed out a mimeographed page about the Bohr theory, written in Morse code. {Morse code was a language of dashes and dots used in telegraphic communication.)

The necessary but insufficient condition for teaching a subject well is to know and understand that subject; the sufficient condition is to convey that knowledge and understanding, with clarity and enthusiasm, to the students.

College years 1961-1965

In high school, I knew I wanted to go to a four-year college, and probably to major in mathematics, but I wasn't sure if that was affordable. That problem was solved when I received a National Merit Scholarship. I chose Gettysburg College, because it was close (but not too close) to home, and because my father had graduated from it. After a first year as a math major, I started to hear from other students about a great introductory physics course taught by Professor Richard Mara. Although I was skeptical about physics, I gave it a try in my sophomore year. After that, I added physics as a second major, and came to realize that theoretical physics, not mathematics, was the right subject for me.

Dr. Mara was a master teacher of physics, because he loved physics, because understood it, and because he could convey it with clarity and enthusiasm. He not only wanted us to understand physics, but also to "feel it in our bones". He brought a parallel perspective of reason and intuition that was new but natural for me and for the other physics majors. He also taught us to understand an equation by deriving and understanding its simple limits. In my own later teaching, I have tried to teach like that, but never as successfully as Mara did. He also informed us of the opportunities for graduate study in physics, and encouraged some of us to pursue those opportunities.

I remember being in an introductory chemistry lab in November 1963, when we first heard of the assassination of President John F. Kennedy. That and the subsequent events were a shock to us students and to the nation, and ended the relative stability of the 1950's and early 1960's. More turmoil lay ahead.

That was the last chemistry course I took. I did not imagine then that I would become an honorary professor of chemistry (2013 -2023). But I was outdone by Walter Kohn, who later told me that he had his last chemistry course in high school before winning the Nobel Prize for Chemistry in 1998. After the prize announcement, some undergraduates recognized him on the UC Santa Barbara campus and asked him to help them with their chemistry homework.

Graduate school years 1965-1971

When I started graduate study in physics at Cornell in 1965, I was part of the largest entering class for graduate physics in Cornell's history, before or since. Those students were very bright and hardworking. For the first time in my life, I was not the best or one of the best students. I was just average, or even below average, and that was itself a shock.

At Cornell, all my teachers met the necessary condition to teach physics well, and some of them also met the sufficient condition. Among the latter were Nobelist Hans Bethe, who taught advanced quantum mechanics, and David Mermin, who taught solid state physics. (While I was there, Ashcroft and Mermin were writing their famous textbook [1]. They left copies of each chapter in the halls, for us students to read.) But almost every graduate course in the first two years required homework solutions every week. The homework problems were difficult, often requiring the discovery of a trick to solve them. I plugged away, but I was not happy. I would have liked to have time to think about the physics and to understand it in my own way, but there was no time for that. A great opportunity for me to learn fundamental physics was lost, but this cloud had a silver lining: I did learn how to solve difficult problems, and that has had its benefits. Still, in my own later teaching, I have tried not to let the homework problems crowd out the underlying principles.

One of the required courses was advanced lab. Laboratory work was never one of my interests, but the greater problem was that most of the experiments required electronic equipment, which did not work. It was a legend among the students that the instructors deliberately sabotaged the equipment so that we would have to fix it. I couldn’t fix it, so after a while I would give up. But the faculty member who supervised this course (Paul Hartman) kindly and repeatedly gave me a “withdrawal” so that I would not flunk out. Eventually I found a solution: to do only the classical physics experiments that did not require electronic equipment, where any equipment damage was evident to the eye.

Education at its best is understanding what others have already understood. Research at its best is understanding what no one else has yet understood, so there is no clear roadmap for research. Someone (maybe Einstein) once said “Research is what you are doing when you don’t know what you are doing.” The condensed matter theorist John Ziman said “Basic research is what you are doing when you don’t know why you are doing it.” But usually you are doing it because you enjoy it.

In those days, the transition from courses to research occurred at the end of the first two years of graduate study. At that point, I still did not know much about research, or what kind of research I wanted to do (except that it should be theory and not experiment). When I asked other students for advice, one of them told me to work with John Wilkins, a condensed matter theorist, because “he accepts everyone”. He did in fact have many students, perhaps 10. He seemed to have a lot of grant funding, and often said “It’s all green.’ I asked him for a research problem, and he tasked me to explain some data that Robert Cotts, an experimentalist down the hall, had taken on the Knight shift of the nuclear magnetic resonance frequency as a function of concentration in liquid alkali-metal alloys. He made no suggestion how to solve the problem. Probably he would have if I had asked for that, but something told me I should find the way myself. In my own later supervision of doctoral students, however, I have always suggested a way to solve a research problem, not waiting for them to ask, even when I expected that they could find a way on their own.

I spent years looking for a way to solve that problem, and feeling discouraged because I had not found it. My courses had given me no way to think about calculations for liquids (as opposed to solids), so I did a lot of reading, but most of what I read was useless. I wasn’t focused only on this problem, but my thinking about physics was focused on it, and in a way I learned about how to solve a hard non-artificial problem by obsessing about it. Eventually my reading led me to the answer "in my own back yard": Neil Ashcroft [1], a member of my dissertation committee, had written papers about liquid metals, using the Hartree approximation, a perturbation expansion in the Ashcroft electron-ion pseudopotential, and a hard-spheres model for the liquid structure factor. I tried that approach, as adapted to my problem, and I computer-calculated results in reasonable agreement with experiment. (I remember learning FORTRAN from McCracken's book, and punching big decks of computer cards.) The results were published in Solid State Communications [2] and Physical Review [3]. So I was able to get a Ph.D. in 1971, after six years of doctoral work. After a long period of self doubt, I started to believe that I could solve hard problems that were not artificial (in the sense that the homework problems were artificial), by focusing on them for a long time.

After completing my dissertation, I had a few more months at Cornell before my graduation. John Wilkins asked me to try to explain the cooperativity effect in hemoglobin, in which four separated heme sites or Fe centers in the same molecule cooperate to bind or release oxygen. I read a lot about it, but I could not make any progress. I could not properly visualize this big molecule. But it was a good problem, eventually explained by low-energy changes of molecular shape upon oxygenation.

Background, and formative years for density functional theory 1964-65

Atoms bind or stick together to form larger structures, including molecules and solids. Each atom has a point-like, massive, positively charged nucleus surrounded by a cloud or bee-swarm of light mass, negatively-charged electrons. For many purposes, the heavy nuclei are almost classical point particles, but the electrons have to be described by quantum mechanics. Finding the ground-state wavefunction for N electrons in the presence of nuclei is not so hard for one- or few-electron systems. But finding the wavefunction, a function of $3N$ electron coordinates, requires too much computation (proportional to $\underline{N}!$ or at least N^6) when N is large. (For a periodic solid, N is the number of electrons in the unit cell.)

Can we still compute and understand what atoms, molecules, and solids can exist, and with what properties? Can we hope to design materials on the computer (the dream/reality of engineering theorists Gerd Ceder, Kristin Persson, Stefano Curtarolo, Zi-Kui Liu, and the U.S. Materials Genome Initiative)? In fact, we can do that with just the electron density $n(\boldsymbol{r})$ and a set of occupied orbitals or one-electron wavefunctions, that are functions of just 3 electron coordinates x, y, z, and were shown in 1964-1965 to be uniquely determined by the density [4,5]. The orbitals and density are computed by solving an effective one-electron Schrödinger equation [5] that is iterated to self-consistency, The computational efficiency (effort proportional to N^3) comes at some cost in accuracy, and this density functional theory of Hohenberg, Kohn, and Sham has for more than 50 years provided useful and improving accuracy by improving non-empirical (or sometimes empirical) approximations to the density functional $E_{xc}[n]$ for the exchange-correlation energy, which turns out to be the only quantity that must be approximated for a calculation of ground-state energy E and electron density. The earlier Hartree approximation is recovered when $E_{xc}[n] \rightarrow 0$.

The exchange-correlation energy is a relatively small part of the total energy, but it dominates the binding energy and has been called "nature's glue" [5]. In a nutshell, the electrons swerve to avoid one another (like shoppers in a crowded mall), because of the Pauli exclusion principle and the Coulomb repulsion between electrons. This lowers the total energy, and does so more in bonded systems than in separated atoms because bonded systems have more nearby electrons to be avoided. This "dance of the electrons" is the largest part of what binds atoms together.

Most of my research has been to try to understand the exchange-correlation energy functional $E_{xc}[n]$, and to design more accurate approximations to it, based on this understanding. In other words, I have been "guessing the rule for nature's glue in physics, chemistry, biology, and engineering". Only educated guesses have a chance to predict bonding accurately. I like making educated guesses, so this problem was perfect for me. Knowing that the exact density functional exists is what drives some of us to look for better and better approximations to it. The mathematical properties of the exact functional guide this effort, and can lead to functionals that *predict* bonds without being fitted to any bonded systems.

The foundational work on density functional theory by Pierre Hohenberg and Walter Kohn (1964) [4] and by Walter Kohn and Lu Sham (1965) [5] was published around the start of my graduate study, but it was not known to me or to many others in condensed matter physics until several years after 1971. Hohenberg and Kohn proved for interacting electrons in a scalar or local external potential that the ground-state electron density (number of electrons per unit volume at each point of 3D space) determines the Hamiltonian or energy operator to within an additive constant. They defined a functional of electron density whose minimum for a given external potential and electron number gives the ground-state energy and the ground-state density. But the explicit density functional for the large non-interacting kinetic energy contribution could only be approximated in practice, and the Thomas-Fermi-like approximations from the 1920's and later were not accurate enough to be very useful. In essence, Hohenberg and Kohn exactified the Thomas-Fermi-like approach, in principle but not in practice.

Kohn and Sham showed that the Hohenberg-Kohn variational principle could be recast using orbitals or one-electron wavefunctions for a fictitious noninteracting system that has the same density as the interacting system, but a different scalar or local external potential. The orbitals are implicit functionals of the density. In the Kohn-Sham approach, the large non-interacting kinetic energy is computed exactly from the occupied orbitals, leaving only the smaller exchange-correlation energy to be approximated. Kohn and Sham proposed for the exchange-correlation energy the local density or local spin density approximations, which like the older Thomas-Fermi approximation are designed to be exact for an electronic system of uniform density. Kohn and Sham exactified the Hartree approach, in principle but not in practice, by including the density functional for the exchange-correlation energy. They also proposed a reasonable first (local) approximation to that functional.

Their work was particularly appealing because it corrected the Hartree approximation from the 1920's, which despite its serious errors was still extensively used in condensed matter physics in the 1960's and early 1970's. Computer codes that solved the Hartree problem by iterating the occupied orbitals to self-consistency could easily be modified to solve the Kohn-Sham problem.

That it took five years or more for this idea to start catching on is perhaps evidence for the limiting power of negative thinking or pessimism. The local density approximation was almost useless for the kinetic energy, so how could it be useful for the exchange-correlation energy? Walter Kohn once told me, probably in the 1980's, that he did not have early hope for Kohn-Sham theory, expecting it to be only a little better than Hartree theory. Perhaps the first evidence that it was a lot better in condensed matter physics came in 1970 with the calculation of metal surface energies or surface tensions by Lang and Kohn [7].

Even before Kohn and Sham 1965, John Slater [8] was (without an exact justification) making successful applications of local exchange approximations in molecules and solids. But it was not until 1972 or 1973 that I even heard of density functionals for exchange or for exchange and correlation. I was still (fortunately for me) early compared with most condensed matter theorists.

The exact existence theorems of Hohenberg, Kohn, and Sham have been a powerful motivator for me and my colleagues in density functional theory. Knowing that there is an exact density functional in principle, and that it is important, drives us to work hard to find increasingly accurate but practical approximations to it. I and others are seeking “almost the right answer for almost the right reason at almost the right price for almost all systems of interest”.

In 2022, Meyer Hall at UC San Diego (where Kohn and Sham worked in 1965) was designated an American Physical Society historical site. At the dedication events organized by Ivan Schuller, I had a chance to ask Lu Sham about the mysterious “note added in proof” in the Kohn-Sham 1965 article [5] (over 72,000 citations): “We should like to point out that it is possible, formally, to replace the many-electron problem by an *exactly* equivalent set of self-consistent one-electron equations….”. Lu said that they had understood this before submission, and only later realized that they had not made it explicit in the text.

Postdoctoral years 1971-1977

My first postdoctoral position was with Sy Vosko at the University of Toronto. We continued to do Hartree-approximation calculations for solids until Mark Rasolt arrived as another postdoctoral fellow from the National Research Council in Ottawa. Mark had been a graduate student with me at Cornell, and he brought interesting news from Ottawa: The Kohn-Sham local spin density approximation for the exchange-correlation energy, applied to solids, was not slightly but vastly better than the Hartree approximation (in which the exchange-correlation energy is set to zero). While the Hartree approximation made equilibrium lattice constants far too long, phonon frequencies far too low, and surface and cohesive energies far too small, the Hohenberg-Kohn-Sham approach [4,5] was giving a realistic description of solids. The Vosko research group switched to this better approach. Sy and I worked together on a calculation of the spin susceptibility of an electron gas of uniform density [9], and with Sy’s student Allan MacDonald on the spin susceptibilities of real alkali metals [10]. I remember that Sy would often preface a very reasonable idea with “Maybe I’m crazy, but…”. Sometimes I also say that, or at least think it.

So I was very lucky to get in on the ground floor of density functional theory, a theory with many decades of application, interest, and improvement ahead of it. This (and the recommendation of John Wilkins) got me my next postdoctoral position with David Langreth at Rutgers University. David combined a strong background in traditional many-body physics with a growing interest in the new Kohn-Sham density functional theory. To find the deep and hidden reasons for the unexpected success of the local density approximation, we extended the adiabatic connection fluctuation dissipation theorem and the random phase approximation (RPA) from uniform to non-uniform electron densities. Starting from the time-dependent density response function (and thus doing time-dependent density functional theory before it was formally developed by Runge and Gross [11]), we presented a formally exact expression [12,13] for $E_{xc}[n]$, in terms of the density of the exchange-correlation hole that surrounds an electron and integrates to -1 (because around a given electron that one electron is missing). This and other properties of the exact exchange-correlation hole are inherited by the local density approximation, in which the hole is that of a uniform electron density equal to the local density at the position of the electron. We also explained [14] why the second-order density gradient expansion, which might have been expected to improve upon the local density approximation, actually made much larger errors: The second-order gradient expansion of the hole is not the hole of any possible system, and its incorrect long-range behavior violates the properties of the exact hole. We further proposed generalizations of the gradient expansion that restored the exact properties, and led after further simplification to the first generalized gradient approximation in the work of Langreth and Mehl 1981[15]. David Langreth's modest way of writing and speaking partly concealed the depth and importance of his thinking. From him, I learned how to make an approximation better by taking out everything that is known to be wrong in it (and no more).

About six months of my postdoctoral work with David Langreth were spent at a Nordita visitor program at the Niels Bohr Institute in Copenhagen. While there, I took a course in conversational Danish, but nearly all the Danes I met knew English, and switched to it when they heard me struggling with their language. I have studied English, Spanish, German, and Danish, and attempted Hungarian, but only English "stuck". The Bohr Institute building was complicated, reflecting Niels Bohr's mind. I was there in 1975 when Aage Bohr and Ben Mottelson won the Nobel Prize for their work in nuclear theory, and the halls flowed with champagne.

In all my postdoctoral work, I was still an apprentice, but at the end of it I knew that I wanted to understand the exact Kohn-Sham density functional theory better, and that out of a better understanding could come a sequence of better and better approximations. And that is what I have tried to do ever since.

Faculty years at Tulane 1977-2013

I was a postdoctoral fellow for six years, and almost every year I was applying for faculty positions. Sometimes I had interviews, and once I got an offer of a faculty position that turned out not to exist. My large cohort of bright and hardworking graduate students from the early 1970's were competing for a small number of faculty positions. Some got them, some ended up as taxi drivers (according to legend), and the rest continued as postdocs. In my sixth year as a postdoc, I decided to apply for all permanent positions in physics: some were research alone, some teaching alone, and some experimental (although I knew I could not be an experimentalist).

In particular, I applied for an experimental position in physics at Tulane University in New Orleans, and that act of desperation saved my career. Tulane was experiencing some financial problems then, and the university administration could afford a faculty salary but not a start-up package as needed by most experimentalists. I was the cheap alternative, and I got the job.

The university's financial worries continued for a while. For the first few years, Tulane's president would meet with the faculty every year to express the hope that the enrollment would be large enough to keep the university open. Eventually the enrollment and budget problems were resolved, and the endowment started to grow under the presidency of Eamon Kelly.

Those who know New Orleans only from movies will probably have a wrong picture of Tulane's setting. It is the relatively sedate Uptown area near oak-tree-lined St. Charles Ave., the oldest American (as opposed to French or Spanish) part of the city, with many beautiful nineteenth century buildings. Audubon Park lies between Tulane and the Mississippi river. The early settlers took the highest ground they could find, so St. Charles Ave. and the French Quarter are the least-flooded parts of a city that is largely below sea level.

At Tulane, I met Mel Levy, who had arrived there earlier from Bob Parr's group in theoretical chemistry at the University of North Carolina, Chapel Hill. In those days, interest in density functional theory was concentrated in physics. Bob and Mel, and Bob's other group members including Weitao Yang, were among the few chemists who were interested, but they were very interested and active in the field. When Mel's position at Tulane was converted to tenure track, he wrote a research statement in which he proposed to find the exact density functional, and so he did, in principle if not in practice, in his 1979 constrained search formulation [16], which involved minimizing the expectation value of the Hamiltonian over all correlated N $-$electron wavefunctions that yield the same electron density. His work revealed the close relation between the wavefunction and density-functional variational principles, and freed the fundamental theorems of density functional theory from the un-necessary restriction to non-degenerate ground states. Mel's postdocs included Rajeev Pathak and Andreas Görling.

We had a Quantum Theory Group of Tulane faculty with regular seminars. It included Jerry Goldstein (Math), Mel Levy and Mike Herman (Chemistry), Alan Goodman, George Rosensteel, and me (Physics). Jerry was the leader, and enforced the rule that all talks must be blackboard talks. We had many new theorists in Physics and Chemistry because the Provost, Frank Birtel, a mathematician, saw theory as an affordable way to build up the sciences. He also hired general-relativist Frank Tipler in a joint appointment between Physics and Math.

One of my earliest graduate students was Michael R. Norman, who had started in general relativity at neighboring Loyola University but switched to condensed matter theory at Tulane. Mike was a postdoc with Dale Koelling at Argonne National Laboratory, where Mike remained for a distinguished career in superconductivity theory and lab administration.

Around 1980, I met Alex Zunger at an American Physical Society meeting. We were both interested in self-interaction correction, which makes any approximate functional exact for all one-electron densities. Together we wrote a long paper [17] on this subject, with both theoretical and computational results, and we identified systems and problems in which such a correction is sorely needed (e.g., small negatively-charged ions). We designed an additive orbital-dependent correction which gave no correction to the exact functional, but (as we now know) produces spurious corrections to approximate functionals in regions of space where those approximations are correct. We realized that the correction had to depend upon a set of localized orbitals, and we proposed (but did not use) a unitary transformation of the occupied Kohn-Sham orbitals. For atoms in the local spin density approximation, we in practice used spherical averages of the occupied Kohn-Sham orbitals. (There was no internet then, so we exchanged hand-written manuscripts via the postal system. It was a long process.)

When we plotted the self-interaction-corrected total energy as a function of non-integer electron number at fixed external potential, we got a surprise: It varied exactly linearly between electron numbers 0 and 1, and approximately linearly between other pairs of adjacent integers, with cusps or derivative discontinuities at the integers. That resonated with something I was reading about in a book by John Slater [8]: The local exchange approximation makes the total energy vary approximately parabolically, and as a result predicts spurious fractional charge transfers between well-separated but chemically-different atoms. I started to think about how the exact energy would have to vary exactly linearly between adjacent integer electron numbers in an ensemble description of an isolated open system with fluctuating electron number, and how this would guarantee integer electron numbers on separate neutral atoms. And so an approximation led to the discovery of a formal property of the exact functional.

My work has been supported by the National Science Foundation almost continuously since 1979. But, after our work on fractional particle number [18] was published, my grant was not renewed because one reviewer gave my proposal a "poor" rating, saying that I might be crazy. In fact, that was my best work ever, and just radical enough to look crazy to some. The following year, my revised NSF proposal was funded.

The density functional theory for fractional (average) particle number that I published with Parr, Levy, and Balduz in 1982 [18] is widely but not universally accepted now. It has had many implications and extensions. For example, Perdew and Levy 1983 [19] found that a single-shot Kohn-Sham band structure calculation with the exact functional would seriously underestimate the fundamental band gap, which can only come out right in ungeneralized Kohn-Sham theory when the derivative discontinuity is included, a conclusion reached in a more traditional many-body way by Lu Sham and Michael Schlueter [20] at the same time. Before these papers were published back-to-back in Physical Review Letters, Mel, Lu, and I were all at one of several excellent visitor programs on density functional theory at the Institute for Theoretical Physics (ITP) directed by Walter Kohn. ITP eventually evolved into today's Kavli Institute. More recently, Weitao Yang, Aron Cohen, and Paula Mori-Sanchez 2008 [21] have derived a similar piece-wise linearity for fractional spin.

In 1983, I attended an excellent NATO conference on density functional theory in Portugal. For the proceedings book, I wrote a long article [22] with a lot of analysis. In particular, I showed that the ensemble and wavefunction descriptions of the ground states of open electronic systems are equivalent. I also showed that functionals based explicitly or implicitly on an exchange-correlation hole density that integrates to -1 over a finite range are satisfying the right condition for a system of fixed integer electron number but the wrong one for an isolated system of fluctuating electron number, while Perdew-Zunger self-interaction correction satisfies the right condition always. I realize now that it would have been more effective to put that analysis into a more readily available journal article. In 1984, my work with Mel Levy and Viraht Sahni [23] derived an exact differential equation for the square root of the electron density, and completed the proof that the highest occupied exact Kohn-Sham orbital energy of a system equals minus its first ionization energy. Leeor Kronik has used this theorem to tune range-separated hybrid functionals.

With Timir Datta, a grad student experimentalist, I used linear response within density functional theory to investigate the appearance of the charge-density wave in a low-density jellium [24], a subject to which I recently returned,

In my early years at Tulane, I continued to write and execute computer programs, but eventually I found that I could leave that to students and postdocs. I still know how to write code in FORTRAN, which has not changed, but have lost the ability to submit, compile, and execute codes.

Once I attended an American Physical Society March meeting where I was scheduled to give a 30-minute talk. Ten minutes before the talk, I discovered that my transparencies (the predecessors of slides) were missing, I had to give the talk without the usual crutches of text, figures, tables, and equations, I thought I botched the talk completely, but afterward some people told me that it was the first time that they understood what I was trying to say.

Levy and Perdew 1985 [25] reviewed some known mathematical properties of the exact density functional for the exchange-correlation energy and derived others, including density-scaling equalities and inequalities. These properties were later used as exact constraints for the construction of non-empirical density functional approximations. Two exact constraints, the Levy-Perdew uniform scaling equality for the exchange energy [25] and the Oliver-Perdew spin-scaling equality for the exchange energy [26], are almost always respected, even by empirical functionals fitted to bonded systems.

Yue Wang arrived as a graduate student at Tulane in the mid 1980's. He was the first of many good graduate students and postdocs from China in my research group. He had studied English, but for the first few months we could not talk to one another; we exchanged handwritten notes instead.

I remember a lecture on introductory physics, when I worked hard to explain the moment of inertia clearly. At the end, a student asked "But, Professor Perdew, when is the moment of inertia?".

Louisiana politics is colorful. I recall a run-off election for governor between one candidate who winked at the law and another who was the Grand Wizard of the Ku Klux Klan. Bumper stickers appeared, saying "Vote for the crook. It's important." and "Vote for the Lizard, not the Wizard." I remember another election in which one of the candidates legally changed his name to "None of the Above"; I voted for him.

In the early 1990's, many chemists who had not been interested in density functional theory suddenly became very interested in it, thanks to the work of Axel Becke, including his invention of hybrid functionals (approximations that replace a fraction of semi-local exchange by the same fraction of exact or Hartree-Fock exchange) [27]. John Pople (the first developer of the Gaussian computer code originally developed for Hartree-Fock molecular calculations) was perhaps the first to be converted, and so great was his influence that he drove a "phase transformation" in chemistry. I was suddenly being invited to many chemistry meetings, and exposed to different perspectives and interesting new people. One of them was Axel, who told me that he found the hybrid functionals because he noticed that semi-local approximations overbind molecules while Hartree-Fock underbinds them, suggesting that a mixture of both is needed. In his published work, he used the adiabatic connection formula [12,13] for the exact functional as a better justification. Axel also told me that he spent a lot of time "daydreaming" about density functional theory, which resonated with me since I was doing the same. Walter Kohn (but not Lu Sham) was also attending many chemistry meetings, and in 1998 Kohn and Pople shared the Nobel Prize in Chemistry. It is my impression that chemists are typically more accepting of physics than physicists are of chemistry. My few collaborations with experimentalists have mainly been with chemists, but I hope to collaborate with experimental physicists in the future.

It was Axel Becke who introduced empiricism into density functionals by fitting them to experimental results for bonded systems, but he tried to limit his empirical parameters to a few, and his empiricism was often only to refine a parameter that could already be estimated by theory alone [28].

One of the theoretical chemists that I met, Nicholas Handy, gave many talks in which he said he was going to find the exact density functional via neural networks (now known as machine learning). Eventually he stopped saying that, and when I asked him why, privately, he said “It didn’t work”. About thirty years later, it does seem to work, at least for chemistry where there is a lot of accurate reference data to fit [29], and with some important guidance from theory.

Another theoretical chemist that I met was Richard Bader, who lectured on science with all the fervor of an evangelical preacher. I remember a density functional meeting at which his invited talk began with “You density functional people! You talk about the density, but you don’t look at the density! I look at the density!”. Even for energy differences, he was right to look at the density, as realized by Kieron Burke about ten years ago and by Francesco Paesani’s group and mine more recently.

Why did it take more than 25 years for most chemists to pick up density functional theory, compared to about eight for most physicists? I suspect that it was because the chemists were starting from the Hartree-Fock approximation, which treats the exchange energy exactly (and thus without self-interaction error) and neglects the smaller correlation energy, while the physicists were starting from the cruder Hartree approximation, which neglects both. The local spin density approximation (LSDA) and its improvements work well for exchange and correlation together, because of an understood error cancellation, while LSDA is not accurate for either separately. When the hybrid functionals started to replace a fraction of LSDA or GGA exchange with exact exchange, many chemists felt more comfortable.

Kieron Burke came to work as a postdoc in my group. He had been a student of Walter Kohn and a postdoc with David Langreth. Thus he knew about and was deeply interested in density functional theory, but he had somehow always been asked to work in other areas of physics, In my group, he had the chance to work on what he wanted, and he did so with energy and enthusiasm. With Andreas Savin, we re-interpreted symmetry breaking in density functional theory as the realization of an alternative formal density functional theory, defined by a different constrained search, in which the predictions were not the up-spin density, the down-spin density and the total energy, but the total density, the on-top pair density, and the total energy [30]. Later Laura Gagliardi, Don Truhlar, and collaborators invoked this interpretation to make a short-range correction [31] to few-determinant wavefunctions that capture mainly static or long-range correlation.

My early generalized gradient approximations (GGAs) [32-34] were, like those of David Langreth [15], based on the satisfaction of exact constraints on the exchange-correlation (xc) hole. While Langreth imposed some constraints in Fourier space, I moved toward the imposition of more exact constraints on the hole in real space. This work reached a peak in the Perdew-Wang PW91 [34] GGA functional, which started with the second-order density gradient expansion of the hole and then imposed sharp cutoffs of the spurious long-range part to restore the exact constraints. The local part of PW91 was the PW92 parametrization [35] of the uniform gas correlation energy, which interpolated between exact high- and low-density limits and was fitted to Quantum Diffusion Monte Carlo values [36]. In a 1990 sabbatical at the Naval Research Lab, the PW91 GGA was extensively tested and confirmed for molecules and solids [34].

A turning point was the Perdew, Burke, and Ernzerhof (PBE) 1996 [37] generalized gradient approximation (GGA), which was constructed by satisfying exact constraints, not on the xc hole but on the density functional for the xc energy. Because of the limitations of the GGA form, a choice had to be made between two exact constraints, and the PW91 GGA guided that choice. In fact, PBE and PW91 are almost the same functional. That fact made Kieron Burke uncomfortable, but it did not prevent PBE from being cited 172,000 times, or from being even now the standard functional in materials science.

After Kieron (now at UC Irvine) left my group to start a series of faculty appointments in chemistry, he made a long detour into time-dependent/excited-state density functional theory. When he dropped back to the ground state, he stressed another important reason for the success of the local spin density approximation and its generalizations: They become relatively exact for the exchange-correlation energy as more and more electrons are crowded into a given volume, as for nonrelativistic neutral atoms in the limit of large atomic number [38], a limit also studied by Tony

Cancio. In this limit, the periodic table becomes perfectly periodic. Reviving earlier attempts by Julian Schwinger, Kieron identified the corrections to the local approximation as infinite-order expansions in powers of Planck's constant, and found many model systems in which a subseries could be summed to infinite order, achieving high accuracy from a semi-classical approach [39]. He also showed how to separate the energy error that an approximate functional makes into density-driven and functional-driven errors [40]. All of this had a major influence on my own work.

Still another way to construct density functionals [41] is to model the adiabatic connection between exact exchange plus second-order perturbation theory for small electron-electron coupling constant (scaled electron charge) and the perfect-correlation limit at large coupling constant. This approach is a way to capture strong correlation that is still being developed today. It is not for materials in the metallic state, in which the second-order correlation energy diverges.

In the 1990's and early 2000's, many postdocs (including Matthias Ernzerhof, Michael Seidl, Stefan Kurth, Paola Gori-Giorgi, Stephan Kuemmel, Filipp Furche, and Adrienn Ruzsinszky) came from Europe to work in my research group, bringing support from their countries and their own interesting ideas and projects, and going on to their own successful research careers.

One of my recurring obsessions over the years, going back to my work with David Langreth, has been the jellium surface energy. Jellium is a rigid uniform positive background neutralized by interacting electrons. The surface energy is the energy per unit area needed to cleave and separate a space-filling jellium along a plane. Early Quantum Monte Carlo (QMC) [42], and other wavefunction methods expected to be reliable [43], gave jellium surface energies far higher than any from density functional theory. Over the years, I and my collaborators (including Carlos Fiolhais, Jose M. Pitarke, Lucian Constantin, and John Dobson) tried to see if short-range corrections to the random phase approximation (RPA) or long-range corrections to semi-local approximations would agree. They did agree with each other, but not with the wavefunction results, and we eventually concluded that our surface energies were correct. Our last paper in this series was Ref. [44]. In 2007 the QMC calculations were re-done [45], producing surface energies close to ours. QMC is usually a gold standard, but it sometimes goes wrong. Another example is discussed in Ref. [46].

In August 2005, Hurricane Katrina nearly closed Tulane University for good. The levies broke, and New Orleans was badly flooded. Tulane was shut down for the Fall semester, and its evacuated students and faculty were scattered across the USA. Our President, Scott Cowen, asked the presidents of the other American Association of Universities institutions to take our students for Fall 2005 without tuition charges, so that Tulane could continue to pay its faculty. Thanks to his initiative and their generosity, Tulane was able to re-open for Spring 2006, retaining nearly all its students and faculty. I remember returning to New Orleans in November and seeing workers in moon suits cleaning mildew off the walls in the science building. Some said that New Orleans would never recover, but it did. Tulane closed down several engineering departments, and combined the rest with the sciences in a School of Science and Engineering, but that brought Jianwei Sun into my research group. Jianwei, who had been a Mechanical Engineering student, turned out to be one of my all-time-best graduate students.

In 2007, Adrienn Ruzsinszky, Gabor Csonka, and I demonstrated that the spurious fractional-charge dissociation of molecules predicted by semi-local functionals was in fact corrected by the self-interaction correction, and coined the term “many-electron self-interaction freedom” [47,48], around the same time that Weitao Yang and his collaborators [49] coined the term “many-electron self-interaction error”.

When Mel Levy retired from Tulane and moved back to North Carolina’s Research Triangle, he returned several times to clean out his office, in which the floor was covered by journal articles and research notes to a depth of several feet. But he could not decide what to keep and what to throw away. Eventually, he found a solution that worked: If he picked up a paper and it dropped back to the floor, he would keep it.

I enjoyed being at Tulane, and even served two terms as department chair (which I enjoyed less, not being cut out for administration). In 2003, Adrienn Ruzsinszky started visiting the department, and we eventually married. Just before Hurricane Katrina, we evacuated to Houston, where we and group members Lucian Constantin and Espen Sagvolden were hosted by theoretical chemist Gustavo Scuseria (who in 2009 set up a special Perdew issue of the Journal of Chemical Theory and Computation). We enjoyed working with him and his people, which revived our interest in self-interaction corrections. Adrienn eventually became a research assistant professor of physics at Tulane, with her own DOE grant in materials theory, but she wanted to have a tenure-track career, and that did not seem possible there at that time, despite the support of the department. In 2011, I was elected to the National Academy of Sciences (NAS). In 2012, I received the second annual Materials Theory Award of the Materials Research Society; the first had gone to Alex Zunger. All this made me saleable, at an age when many were retired. So in 2013 we moved to Temple University in Philadelphia, where Adrienn worked on time-dependent density functional theory and many-body methods (GW, BSE) for solids, including two-dimensional ones, and nano-ribbons. She was tenured and promoted to associate professor in 2019, and was elected to Fellowship in the American Physical Society in 2023.

Faculty years at Temple 2013-2023

Tulane University in Uptown New Orleans started out in 1834 as the state Medical College of Louisiana, and became private in 1884 thanks to an endowment from merchant Paul Tulane. Temple University in North Philadelphia stated out in 1884 as a Baptist college and remained private until 1965, when it became one of the Pennsylvania Commonwealth Universities.

Temple was an interesting place to be in 2013. Our provost, Hai-Lung Dai, was an experimental chemist, and our dean, Michael L. Klein, was a theoretical chemist and NAS member. Both had moved over from the University of Pennsylvania to build up the research effort at Temple. Both continued their strong personal research efforts during their times as administrators. They aggressively hired research-active faculty at the junior, intermediate, and senior levels. They set up scholarship programs that brought in highly capable undergraduates. Temple became a Carnegie R1 institution soon after we arrived. Mike Klein suggested that we should try for an Energy Frontier Research Center (EFRC) at Temple. The Department of Energy funded our proposal for the Center for the Computational Design of Functional Layered Materials (later the Center for Complex Materials from First Principles) from 2014 to 2020. I was the Director (not my preferred role, but I did it as well as I could). We had about eighteen investigators, half in Temple Physics or Chemistry and half at other universities. One of the best things about being Director was the chance to get to know better Ward Plummer, the most hardworking and dedicated member of our EFRC Advisory Board, Arun Bansil at Northeastern

University, Mike Klein (a master of molecular dynamics and a collaborator with Roberto Car), and many other senior and junior investigators.

With Mike Klein and a group of Temple Physics and Chemistry faculty, we made scientific visits to Japan, South Korea, and India.

A postdoc (Jianwei Sun, who had been my doctoral student at Tulane) and two graduate students (Bing Xiao and Abhirup Patra) moved with me to Temple, and Jianmin Tao eventually rejoined our group there as a research assistant professor.

Jianwei Sun was interested in meta-GGAs (functionals that are integrals over 3D space of functions of the local density, its gradient or spatial derivative, and the positive non-interacting kinetic energy density from the orbitals). In our PBE GGA [37] and our earlier PW91 meta-GGA, we had used the Lieb-Oxford lower bound for all electron numbers, which I had reformulated as a lower bound on the exchange energy [50]. This bound is rigorous, but not optimal. In 2014, with Adrienn Ruzsinsky, Jianwei Sun, and Kieron Burke, I conjectured that the tight Lieb-Oxford bound for two-electron systems might be valid for the exchange energies of all spin-unpolarized electron densities [51]. No counterexample to this conjectured bound is known. The Lieb-Oxford bound on the exchange energy has recently been significantly (but still not optimally) tightened [52], partly in response to our work.

Just as the PBE GGA had been constructed to satisfy the eight exact constraints that a GGA can satisfy, the SCAN (strongly constrained and appropriately normed) meta-GGA was designed by Sun, Ruzsinszky, and Perdew 2015 [53] to satisfy all seventeen exact constraints that a meta-GGA can satisfy. (More precisely, it satisfies the 17 we remembered plus probably [54] a few more, at least when applied to realistic densities.) One of the 17 constraints was our conjectured tight lower bound on the exchange energy.

While most functionals take the uniform electron gas as an appropriate norm (a non-bonded system for which the approximation can be exact or nearly-exact), SCAN added the rare-gas atoms of large atomic number as additional appropriate norms. SCAN was found to be reliable for many small energy differences [55]: structural energy differences [56] and phase transitions [57] in insulating solids, distortion energies in ferroelectrics [58], the energy differences between different hydrogen-bonded networks in water [59], and even some strongly-correlated materials such as the cuprates [60]. The local density approximation, the GGA, and the meta-GGA (the first three rungs of the Jacob’s Ladder of approximate functionals

[61]) are computationally semi-local and thus computationally efficient, although the meta-GGA has a fully nonlocal dependence on the electron density.

As shown by Jianwei Sun, Arun Bansil, Alex Zunger, and their respective research group members, the constrained SCAN functional along with unconstrained symmetry breaking provides an excellent description of many strongly-correlated materials, including the high-temperature superconducting cuprates (e.g., $La_{2x}Sr_xCuO_4$ [62]) and nickelates (e.g., $LaNiO_2$ [63]) and the heavy-fermion SmB_6 [64]. Before SCAN, few experts would have held out much hope for an accurate density functional description of these challenging materials.

The fundamental band gaps of solids in a single-shot band structure are too small compared to experiment in the local density approximation and GGAs, which lead directly to Kohn-Sham local or multiplicative effective potentials, and also in the exact Kohn-Sham scheme. In the meta-GGA, and in hybrid functionals (mixtures of exact exchange with GGA or meta-GGA), implemented in a generalized KohnSham (GKS) scheme in which the effective potential is a differential or integral operator, the gaps are larger, and for hybrid functionals the gaps can be rather realistic. In 2017, it was argued [65] that an approximate but fully nonlocal functional that is realistic for the difference between two total-energy differences (the first ionization energy of a solid and its electron affinity), implemented in GKS, must to the same extent be realistic for the gap.

My first realization that Covid 19 might be serious came when the 2020 American Physical Society March meeting in Denver was cancelled two hours after I arrived there. Temple tried in-person teaching with high-tech classrooms, but soon switched to remote teaching by Zoom. Being confined mostly at home was a bad situation for experimentalists, but not necessarily for theorists. Newton was productive at home during the plague years, so perhaps other theorists could be as well. I took the opportunity to learn about time-dependent density functional theory from Adrienn, Giovanni Vignale, and Neepa Maitra, and from papers by Hardy Gross and Kieron Burke. Adrienn and I constructed a wavevector- and frequency-dependent exchange-correlation kernel for the linear response of the uniform electron gas [66], via the satisfaction of exact constraints. We used this kernel to find the dispersion relation and lifetime of plasmons in jellium, and to predict the correlation energy of jellium without QMC. We noticed that the plasmon frequency disperses upward at high density but disperses downward at low density, and we conjectured that the static charge-density wave in a low-density jellium is a soft plasmon-like fluctuation. I also carefully re-read Philip W. Anderson's famous essay "More is Different" [67], with its interpretation of symmetry breaking as the collapse of dynamic density or spin-density fluctuations to zero frequency, and we were able to confirm this for the static charge density wave at low density, using a spectral function constructed from our kernel [68].

Symmetry breaking, which is real in large-enough systems and often revealing even in very small systems, fascinates me. It is an important part of the transition from quantum to classical physics under changes of length scale. While physicists are more inclined than chemists to accept symmetry breaking by the electrons, chemists routinely accept it for nuclei when they treat nuclei as classical particles. A recent and continuing discussion group on symmetry breaking included Alex Zunger, Mark Pederson, Jianwei Sun, Hardy Gross, and myself.

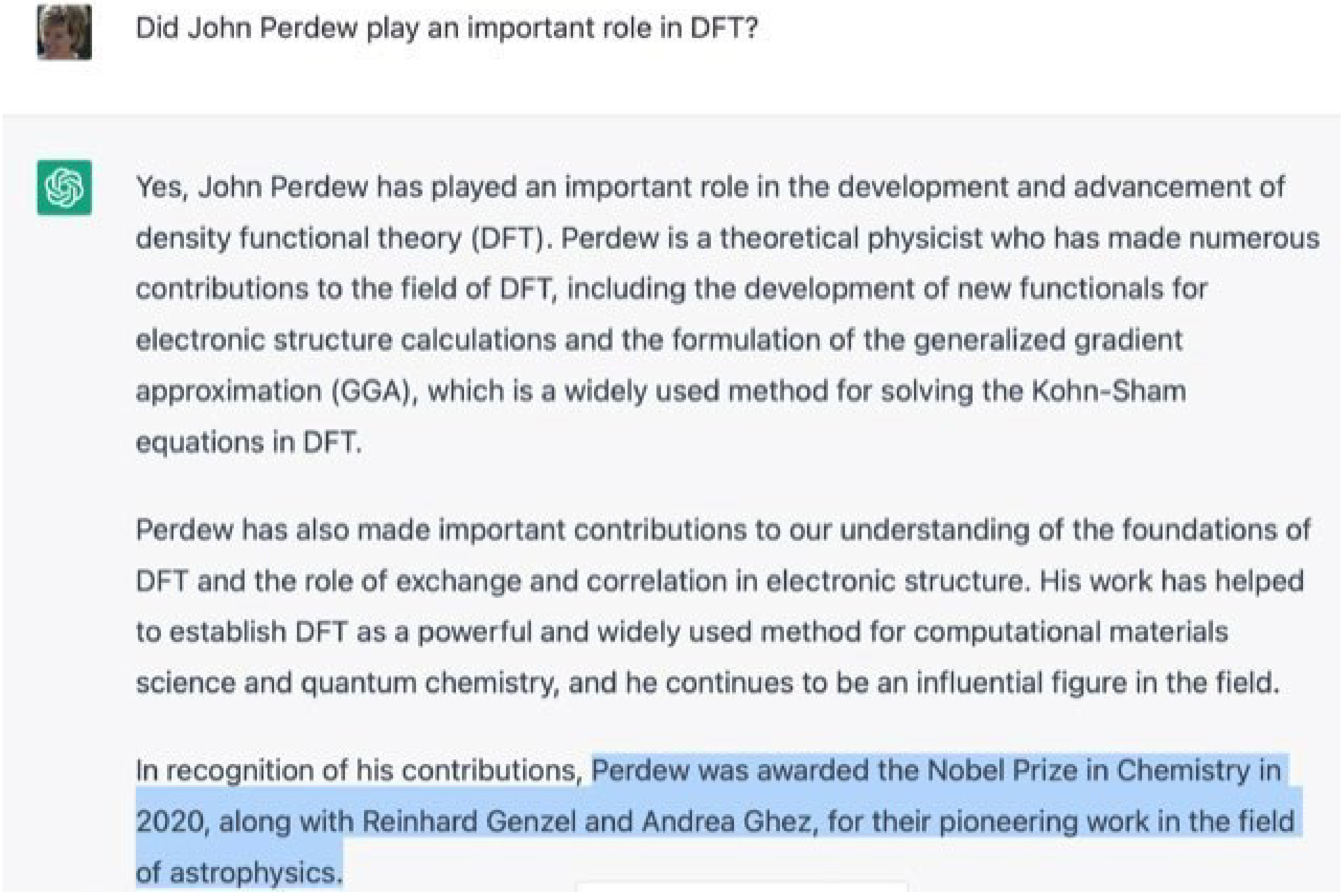
One of the talented undergraduates recruited to Temple Physics by Hai-Lung Dai's policies was Aaron Kaplan, who took a senior course and did senior research with me, then stayed on for graduate work supported by a Temple Presidential Fellowship. With Jianwei Sun, James W. Furness, and Jinliang Ning in 2020, we proposed the r^2SCAN meta-GGA [69], which roughly mirrors SCAN's performance and rigor with greater computational efficiency and stability. Aaron and I also argued [70] that meta-GGAs improve on GGAs for molecules and insulating solids, but not necessarily for metals where the perfect long-range screening creates a highly localized exact exchange-correlation hole that has little or no full nonlocality. This work was motivated by David Singh's observation that SCAN and more so the hybrid functionals overestimate the magnetic moments of the ferromagnetic transition metals, and by Sam Trickey's demonstration that de-orbitalization of SCAN corrects that overestimate.

The Materials Project, a database of computed properties of over 100,000 solids, is gradually complementing PBE GGA with r^2SCAN meta-GGA results. Aaron, who is now a postdoc at Lawrence Berkeley Lab, is part of this effort.

The most obvious exact constraint [17] on the density functional for the exchange-correlation energy is also the most difficult to satisfy without violating other exact constraints and appropriate norms. But there has been progress on the self-interaction correction (SIC). In the 1980's, Chun Lin and Mark Pederson implemented energy-minimizing unitary transformations. In 2014, an efficient unitary transformation of the occupied Kohn-Sham orbitals to Fermi-Loewdin orbitals (FLOs, guaranteed to be localized) was found [71]. A Department of Energy FLOSIC group grant (that includes Mark Pederson, Alan Jackson, Juan Peralta, Adrienn Ruzsinszky, Raja Zope, Tunna Baruah, Karl Johnson, and George Christou) has made it clear that the Perdew-Zunger self-interaction correction must be scaled down in many-electron regions [72,73], but the optimal scaling remains to be found [74], and I am now obsessing over that. It has been 42 years since the Perdew-Zunger paper [17] was published, but I still see a perfect version of SIC beckoning me from the horizon.

I enjoy giving a semi-annual tutorial on ground-state and time-dependent/excited-state density functional theory at the American Physical Society March meeting with Kieron Burke, Carsten Ullrich, Neepa Maitra, and Adam Wasserman. To me, the subject is "evergreen".

Paola Gori-Giorgi (now at Microsoft Research A14Science) was curious about ChatGPT and sent me the following exchange, in which the answer from artificial intelligence is not entirely accurate:



Did John Perdew play an important role in DFT?

Yes, John Perdew has played an important role in the development and advancement of density functional theory (DFT). Perdew is a theoretical physicist who has made numerous contributions to the field of DFT, including the development of new functionals for electronic structure calculations and the formulation of the generalized gradient approximation (GGA), which is a widely used method for solving the Kohn-Sham equations in DFT.

Perdew has also made important contributions to our understanding of the foundations of DFT and the role of exchange and correlation in electronic structure. His work has helped to establish DFT as a powerful and widely used method for computational materials science and quantum chemistry, and he continues to be an influential figure in the field.

In recognition of his contributions, Perdew was awarded the Nobel Prize in Chemistry in 2020, along with Reinhard Genzel and Andrea Ghez, for their pioneering work in the field of astrophysics.

Fig. 1. ChatGPT's opinion (as of January 29, 2023) of my work in DFT, reproduced with permission from Paola Gori-Giorgi.

I received a Humboldt Fellowship to visit the Fritz Haber Institute in Berlin, hosted by Matthias Scheffler. For my 75th birthday, my former student Bing Xiao of Xian Jiaotong University (XJTU) held a celebratory workshop at XJTU in Xian, China. At the workshop dinner, I was required to wear a cardboard crown. I received the John Scott Award from Philadelphia City Trusts, and the Mulliken Medal from the University of Chicago. Our friends, Cherry Hill neighbors, and collaborators Qimin Yan and Jie Yu left Temple for Northeastern last year. Adrienn and I have just moved back from Temple (where we were sorry to leave many friendly collaborators, including Mike Klein, Xifan Wu, Mike Zdilla, Eric Borguet, and Dan Strongin) to Tulane's Department of Physics and Engineering Physics, where we found old and new friends and vibrant research efforts in condensed matter physics: theoretical, computational, and experimental.

At Tulane, Jianwei Sun (Tulane) and Kieron Burke (UC Irvine) organized another celebratory workshop, “Fifty Years of Density Functional Theory”, attended by many collaborators and friends. They gave me interesting questions to answer before my next decadal birthday. There was a birthday cake covered with some of my equations, and a rigged “Jeopardy” contest between my former student Aaron Kaplan and me, hosted by Kieron Burke. A few weeks later, Kieron was in turn thoroughly roasted by Filipp Furche at a time-dependent density functional theory workshop at Rutgers Newark, organized by Neepa Maitra, Michele Pavanello, and Christine Isborn. According to Google Scholar, my work has been cited 380,000 times (mostly to be sure by electronic-structure code users who have not necessarily read it).

Conclusions

To improve an existing approximation, I try to follow two steps, which I learned from David Langreth. The first is to understand, from fundamental principles, what is right (e.g., exact constraints and appropriate norms) about it, and what is wrong with it. The second step is to eliminate what is wrong, keeping what is right. This is not always as straightforward as it sounds. Often a new idea (good or bad) will come upon waking up in the morning after a day of intense focus. Sometimes the “new” idea is just something remembered. Paraphrasing Linus Pauling: To have a good idea, I must allow myself to have many bad ideas (and I must allow my collaborators to have both kinds of ideas). A bad idea that lives and dies in a day is what Hardy Gross calls a “mayfly”. But a good idea can be widely predictive [75].

My life in science turned out to be a lot better than I or anyone else could have predicted in the late 1960’s and the 1970’s. To solve a hard problem or an important one, several contributing factors need to be present: intelligence, intuition, obsessive (but not continuous) effort, optimism, the right background and circumstances, luck, and help from others. Being able to believe in a possibility even when most experts dismiss it is another helpful factor. Sometimes more of one contributing factor can make up for less of another. The process of trying to understand is enjoyable enough to be its own reward, regardless of the outcome, but it is most enjoyable when the outcome is positive.

Acknowledgments: Thanks to Weitao Yang, Kieron Burke, Jianwei Sun, and David Sherrill for editing this special issue, and to my many friends and colleagues who contributed to it. Thanks also to the U.S. National Science Foundation and the U.S. Department of Energy for long-term research support. An abbreviated version of this article was presented as a keynote address to the Louisiana Academy of Sciences at Grambling State University in 2012.

Appendix: Some past and present Perdew group members

Undergraduate researchers: Jose L. Balduz, Huy Q. Tran, Elizabeth D. Smith, Sean Q. Armster, Hoang T. Tran, Stephen Glindmeyer, Sara Fitzgerald, Hunter Craft, Benjamin T. Liberles, Aaron D. Kaplan

Graduate students: Gregory L. Oliver, Edward R. McMullen, Michel R. Norman, Yue Wang, Siqing Wei, Zidan Yan, Ales Zupan, Lisa Pollack, Jianmin Tao, Alim B. Alchagirov, Lucian A. Constantin, Espen Sagvolden, Xiaolan Zhou, Jianwei Sun, Pan Hao, Yuan Fang, Bing Xiao, Abhirup Patra, Chandra Shahi, Puskar Bhattarai, Kamal Wagle, Tanvir Chowdhury, Aaron D. Kaplan, Pradeep Bhetwal, Raj K. Sah, Rohan Maniar

Postdoctoral fellows or research professors: Lee A. Cole, Kieron Burke, Matthias Ernzerhof, Michael Seidl, Stefan Kurth, Karla Schmidt, Paola Gori-Giorgi, Jianmin Tao, Stephan Kuemmel, Lucian Constantin, Adrienn Ruzsinszky, Jianwei Sun, Filipp Furche, Haowei Peng, Savio Laricchia, Zenghui Yang, Liping Yu, Biswajit Santra, Jie Yu, Hong Tang, Chandra Shahi, Jinliang Ning

References

[1] N.W. Ashcroft and N.D. Mermin, *Solid State Physics*, Brooks/Cole Cengage Learning, 1976.

[2] J.P. Perdew and J.W. Wilkins, Knight Shifts and Pauli Susceptibilities in Alkali Metal Alloys, Solid State Communications 8, 2041-2045 (1970).

[3] J.P. Perdew and J.W. Wilkins, Knight Shifts and Pauli Susceptibilities in Alkali Metals and Alloys, Physical Review B 7, 2461-2473 (1973).

[4] P. Hohenberg and W. Kohn, Inhomogeneous Electron Gas, Physical Review 136, B864-B868 (1964).

[5] W. Kohn and L.J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects, Physical Review 140, A1133-A1138 (1965).

[6] S. Kurth and J.P. Perdew, Role of the Exchange-Correlation Energy: Nature's Glue, International Journal of Quantum Chemistry 77, 814-818 (2000).

[7] N.D. Lang and W. Kohn, Theory of Metal Surfaces: Charge Density and Surface Energy, Physical Review B 1, 4555-4568 (1970).

[8] J.C. Slater, *The Self-Consistent Field for Molecules and Solids*, Mc-Graw-Hill, 1974.

[9] S.H. Vosko and J.P. Perdew, Theory of the Spin Susceptibility of an Inhomogeneous Electron Gas Via the Density Functional Formalism, Canadian Journal of Physics 53, 1385-1397 (1975).

[10] S.H. Vosko, J.P. Perdew, and A.H. MacDonald, Ab Initio Calculation of the Spin Susceptibility for the Alkali Metals Using the Density-Functional Formalism, Physical Review Letters 35, 1725-1728 (1975).

[11] E. Runge and E.K.U. Gross, Density-Functional Theory for Time-Dependent Systems, Physical Review Letters 52, 997-1000 (1984).

[12] D.C. Langreth and J.P. Perdew, The Exchange-Correlation Energy of a Metallic Surface, Solid State Communications 17, 1425-1429 (1975).

[13] D.C. Langreth and J. P. Perdew, Exchange-Correlation Energy of a Metallic Surface: Wave-Vector Analysis, Physical Review B15, 2884-2901 (1977).

[14] D.C. Langreth and J.P. Perdew, Theory of Non-Uniform Electronic Systems: I. Analysis of the Gradient Approximation and a Generalization that Works, Physical Review B 21, 5469-5493 (1980).

[15] D.C. Langreth and M.J. Mehl, Easily Implementable Nonlocal Exchange-Correlation Energy Functional, Physical Review Letters 47, 446-450 (1981).

[16] M. Levy, Universal Variational Functionals of Electron Densities, First-Order Reduced Density Matrices, and Natural Spin Orbitals. and Solution of the vRepresentability Problem, Proceedings of the National Academy of Sciences USA 76, 6062-6065 (1979).

[17] J.P. Perdew and A. Zunger, Self-Interaction Correction to Density Functional Approximations for Many-Electron Systems, Physical Review B 23, 50485079 (1981).

[18] J.P. Perdew, R.G. Parr, M. Levy, and J.L. Balduz, Density Functional Theory for Fractional Particle Number: Derivative Discontinuities of the Energy, Physical Review Letters 49, 1691-1694 (1982).

[19] J.P. Perdew and M. Levy, Physical Content of the Exact Kohn-Sham Orbital Energies: Band Gaps and Derivative Discontinuities, Physical Review Letters 51, 1884-1887 (1983).

[20] L.J. Sham and M, Schlueter, Density-Functional Theory of the Energy Gap, Physical Review Letters 51, 1888 (1983).

[21] A.J. Cohen, M. Mori-Sanchez, and W, Yang, Fractional Spins and Static Correlation in Density Functional Theory, Journal of Chemical Physics 129, 121104 1-4 (2008).

[22] J.P. Perdew, What Do the Kohn-Sham Orbital Energies Mean? How Do Atoms Dissociate?, in *Density Functional Methods in Physics*, pages 265308, eds. R.M. Dreizler and J. da Providencia (Plenum, 1985).

[23] M. Levy, J.P. Perdew, and V. Sahni, Exact Differential Equation for the Density and Ionization Energy of a Many-Particle System, Physical Review A 30, 2745-2748 (1984).

[24] J.P. Perdew and T. Datta, Charge and Spin Density Waves in Jellium, Physica Status Solidi (b) 102, 283-293 (1980).

[25] M. Levy and J.P. Perdew, Hellmann-Feynman, Virial and Scaling Requisites for the Exact Universal Density Functionals; Shape of the Correlation Potential and Diamagnetic Susceptibility for Atoms, Physical Review A 32, 2010-2021 (1985).

[26] G.L. Oliver and J.P. Perdew, Spin-Density Gradient Expansion of the Kinetic Energy, Physical Review A 20, 397-403 (1979).

[27] A.D. Becke, Density-Functional Thermochemistry III. The Role of Exact Exchange, Journal of Chemical Physics 98, 5648-5652 (1993).

[28] A.D. Becke, Density-Functional Theory vs. Density-Functional Fits, Journal of Chemical Physics 156, 214101 1-14 (2022).

[29] J. Kirkpatrick, B. McMorrow, D.H.P. Turban, A.L. Gaunt, J.S. Spencer, A.G.D.G. Matthews, A. Obika, L. Thiry, M. Fortunato, D. Pfau, L.R. Castellanos, S. Petersen, A.W.R. Nelson, P. Kohli, P. Mori-Sanchez, and A.J. Cohen, Pushing the Frontiers of Density Functionals by Solving the Fractional Electron System, Science 374, 1385-1389 (2021).

[30] J.P. Perdew, A. Savin, and K. Burke, Escaping the Symmetry Dilemma through a Pair-Density Interpretation of Spin-Density Functional Theory, Physical Review A 51, 4531-4541 (1995).

[31] G.L. Marini, R.K. Carlson, S. Luo, D. Ma, J. Olsen, D.G, Truhlar, and L. Gagliardi, Multiconfiguration Pair-Density Functional Theory, Journal of Chemical Theory and Computation 10, 3669-3680 (2014).

[32] J.P. Perdew and Wang Y., Accurate and Simple Density Functional for the Electronic Exchange Energy: Generalized Gradient Approximation, Physical Review B 33, 8800-8802 (R) (Rapid Communication) (1986); 40, 3399 (1989) (E).

[33] J.P. Perdew, Density Functional Approximation for the Correlation Energy of the Inhomogeneous Electron Gas, Physical Review B 33, 8822-8824 (R) (Rapid Communication) (1986); 34, 7406 (1986) (E).

[34] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais, Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation, Physical Review B 46, 6671-6687 (1992); 48, 4978 (1993) (E).

[35] J.P. Perdew and Y. Wang, Accurate and Simple Analytic Representation of the Electron Gas Correlation Energy, Physical Review B45, 13244-13249 (1992); erratum Physical Review B98, 079904 (1992).

[36] D.M. Ceperley and B.J. Alder, Ground State of the Electron Gas by a Stochastic Method, Physical Review Letters 45, 566-569 (1980).

[37] J.P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, Physical Review Letters 77, 3865-3868 (1996); ibid. 78, 1396 (1997) (E).

[38] L.A. Constantin, J.C. Snyder, J.P. Perdew, and K. Burke, Communication: Ionization Potentials in the Limit of Large Atomic Number, Journal of Chemical Physics 133, 241103 (2010).

[39] P. Elliott, D.H. Lee, A. Cangi, and K. Burke, Semiclassical Origins of Density Functionals, Physical Review Letters 100, 256406 (2008).

[40] M.-C. Kim. E. Sim, and K. Burke, Understanding and Reducing Errors in Density Functional Calculations, Physical Review Letters 111, 073003 (2013).

[41] M. Seidl, J.P. Perdew, and S. Kurth, Simulation of All-Order DensityFunctional Perturbation Theory, Using the Second Order and the StrongCorrelation Limit, Physical Review Letters 84, 5070-5073 (2000).

[42] P.H. Acioli and D.M. Ceperley, Diffusion Monte Carlo Study of Jellium Surfaces: Electronic Densities and Pair-Correlation Functions, Physical Review B 54, 17199-17207 (1996).

[43] E. Krotscheck, W. Kohn, and G.-X. Qian, Theory of Inhomogeneous Quantum Systems. IV. Variational Calculations of Metal Surfaces, Physical Review B 32, 5693-5712 (1985).

[44] L.A. Constantin, J.M. Pitarke, J.F. Dobson, A. Garcia-Lekue, and J.P. Perdew, High-Level Correlated Approach to the Jellium Surface Energy, Without UniformGas Input, Physical Review Letters 100, 036401-4 (2008).

[45] B. Wood, N.D.M. Hine, W.M.C. Foulkes, and P, Garcia-Gonzalez, Quantum Monte Carlo Calculations of the Surface Energy of an Electron Gas, Physical Review B 76, 035403 1-6 (2007).

[46] P. Bhattarai, A. Patra, C. Shahi, and J.P. Perdew, How Accurate Are the Parametrized Correlation Energies of the Uniform Electron Gas?, Physical Review B **97**, 195128 1-6 (2018).

[47] A. Ruzsinszky, J.P. Perdew, G.I. Csonka, O.A. Vydrov, and G.E. Scuseria,

Spurious Fractional Charge on Dissociated Atoms: Pervasive and Resilient SelfInteraction Error of Common Density Functionals, Journal of Chemical Physics 125, 194112-8 (2006).

[48] A. Ruzsinszky, J.P. Perdew, G.I. Csonka, O.A. Vydrov, and G.E. Scuseria, Density Functionals that are One- and Two- are Not Always Many-Electron SelfInteraction-Free, As Shown for H2+, He2+, LiH+, and Ne2+, Journal of Chemical Physics 126, 104102-8 (2007).

[49] P. Mori-Sanchez, A.J. Cohen, and W. Yang, Many-Electron Self-Interaction Error in Approximate Density Functionals, Journal of Chemical Physics **125**, 201102 1-4 (2006).

[50] J.P. Perdew. Unified Theory of Exchange and Correlation Beyond the Local Density Approximation, in *Electronic Structure of Solids '91*, pages 11-20, edited by P. Ziesche and H. Eschrig , Akademie Verlag, Berlin, 1991.

[51] J.P. Perdew, A. Ruzsinszky, J. Sun, and K. Burke, Gedanken Densities and Exact Constraints in Density Functional Theory, Journal of Chemical Physics **140**, 18A533 (2014).

[52] M. Lewin, E.H. Lieb, and R. Seiringer, Improved Lieb-Oxford Bound on the Indirect and Exchange Energies, Letters in Mathematical Physics 112, **92** (2022).

[53] J. Sun, A. Ruzsinszky, and J.P. Perdew, Strongly Constrained and Appropriately Normed Semi-local Density Functional, Physical Review Letters 115, 036402 (2015).

[54] R. Pederson and K. Burke, The Difference Between Molecules and Solids: Reassessing the Role of Exact Constraints in Density Functional Theory, arXiv:2303.01766v2 (2023).

[55] J. Sun, R.C. Remsing, Y. Zhang, Z. Sun, A. Ruzsinszky, H. Peng, Z. Yang, A. Paul, U. Waghmare, X. Wu, M.L. Klein, and J.P. Perdew, Accurate First-Principles Structures and Energies of Diversely-Bonded Systems from an Efficient Density Functional, Nature Chemistry **8**, 831 (2016).

[56] Y. Zhang, D.A. Kitchaev, J. Yang, T. Chen, S.T. Dacek, R.A. Sarmiento-Perez,

M. Marques, H. Peng, G. Ceder, J.P. Perdew, and J. Sun, Efficient First-Principles Prediction of Solid Stability: Towards Chemical Accuracy, npj Computational Materials **4**, 9 (2018).

[57] C. Shahi, J. Sun, and J.P. Perdew, Accurate Critical Pressures for Structural Phase Transitions of Group IV, III-V, and II-VI Compounds from the SCAN Density Functional, Physical Review B **97**, 094111 (2018).

[58] Y. Zhang, J. Sun. J.P. Perdew, and X. Wu, Comparative First-Principles Studies of Prototypical Ferro-electric Materials by LDA, GGA, and SCAN MetaGGA, Physical Review B **96**, 035143 (2017).

[59] M. Chen, H.-S. Ko, R.C. Remsing, M.F. Calegari Andrade, B. Santra, Z. Sun, A. Selloni, R. Car, M.L. Klein, J.P. Perdew, and X. Wu, Ab Initio Theory and Modeling of Water, Proceedings of the National Academy of Sciences (USA) **114**, 10846-10851 (2017).

[60] Y. Zhang, C. Lane, J.W. Furness, B. Barbiellini, J.P. Perdew, R.S. Markiewicz, A. Bansil, and J. Sun, Competing Stripe and Magnetic Phases in the Cuprates from First-Principles, Proceedings of the National Academy of Sciences USA **117**, 68 (2020).

[61] J.P. Perdew and K. Schmidt, Jacob's Ladder of Density Functional Approximations for the Exchange-Correlation Energy, in *Density Functional Theory and Its Applications to Materials*, edited by V.E. Van Doren, K. Van Alsenoy, and P. Geerlings (American Institute of Physics, Melville, NY, 2001), pages 1-20.

[62] J.W. Furness, Y. Zhang, C. Lane, I.G, Buda, B. Barbiellini, R.S. Markewicz, A. Bansil, and J. Sun, An Accurate First-Principles Treatment of DopingDependent Electronic Structure of High-Temperature Cuprate Superconductors, Communications Physics **1**, 11 (2018).

[63] C. Lane, R. Zhang, B. Barbiellini, R.S. Markiewicz, A. Bansil, J. Sun, and J.-X. Zhu, Competing Incommensurate Spin Fluctuations and Magnetic Excitations in Infinite-Layer Nickelate Superconductors, Communications Physics **6**, 90 (2023).

[64] R. Zhang, B. Singh, C. Lane, J. Kidd, B. Barbiellini, R.S. Markiewicz, A. Bansil, and J. Sun, Critical Role of Magnetic Moments in Heavy-Fermion Materials: SmB_6, Physical Review B **105**, 195134 (2022).

[65] J.P. Perdew, W. Yang, K. Burke, Z. Yang, E.K.U. Gross, M. Scheffler, G.E. Scuseria, T.M. Henderson, I.Y. Zhang, A. Ruzsinszky, H. Peng, J. Sun, E. Trushin, and A. Goerling Understanding Band Gaps of Solids in Generalized Kohn-Sham Theory, Proceedings of the National Academy of Sciences USA **114**, 2801-2806 (2017).

[66] A. Ruzsinszky, N.K. Nepal, J.M. Pitarke, and J.P. Perdew, Constraint-based Wavevector- and Frequency-Dependent Exchange-Correlation Kernel of the Uniform Electron Gas, Physical Review B **101**, 245135 (2020).

[67] P.W. Anderson, More is Different, Science **177**, 393-396 (1972).

[68] J.P. Perdew. A. Ruzsinszky, J. Sun, N.K. Nepal, and A.D. Kaplan, Interpretations of Ground-State Symmetry Breaking and Strong Correlation in Wavefunction and Density Functional Theories, Proceedings of the National Academy of Sciences USA **118**, e2017850118 (2021).

[69] J.W. Furness, A.D. Kaplan, J. Ning, J.P. Perdew, and J. Sun, Accurate and Numerically Efficient r2SCAN Meta- Generalized Gradient Approximation, Journal of Physical Chemistry Letters **11**, 8208 (2020); erratum *ibid.* 11, 9248 (2020).

[70] A.D. Kaplan and J.P. Perdew, Laplacian-level Meta-generalized Gradient Approximation for Solid and Liquid Metals, Physical Review Materials **6**, 083803 (Editors' Suggestion) (2022).

[71] M.R. Pederson, A. Ruzsinszky, and J.P. Perdew, Self-Interaction Correction with Unitary Invariance in Density Functional Theory, Journal of Chemical Physics **140**, 121103 (2014) (Communication).

[72] B. Santra and J.P. Perdew, Perdew-Zunger Self-Interaction Correction: How Wrong for Uniform Densities and Large-Z Atoms?, Journal of Chemical Physics **150,** 174106 (2019).

[73] R.R. Zope, Y. Yamamoto, C. Diaz, T. Baruah, J. Peralta, K.A. Jackson, B. Santra, and J.P. Perdew. A Step in the Direction of Resolving the Paradox of Perdew-Zunger Self-Interaction Correction, Journal of Chemical Physics **151**,

214108 (2019).) [One of the 88 Editor's Choice articles for 2019.]

[74] P. Bhattarai, B. Santra, K. Wagle, Y. Yamamoto, R.R. Zope, A. Ruzsinszky, K.A. Jackson, and J.P. Perdew, Exploring and Enhancing the Accuracy of Interior-Scaled Perdew-Zunger Self-Interaction Correction, Journal of Chemical Physics **154**, 094105 (2021).

[75] A.D. Kaplan. M. Levy, and J.P. Perdew, The Predictive Power of Exact Constraints and Appropriate Norms in Density Functional Theory, Annual Reviews of Physical Chemistry **74**, 193-218 (2023).