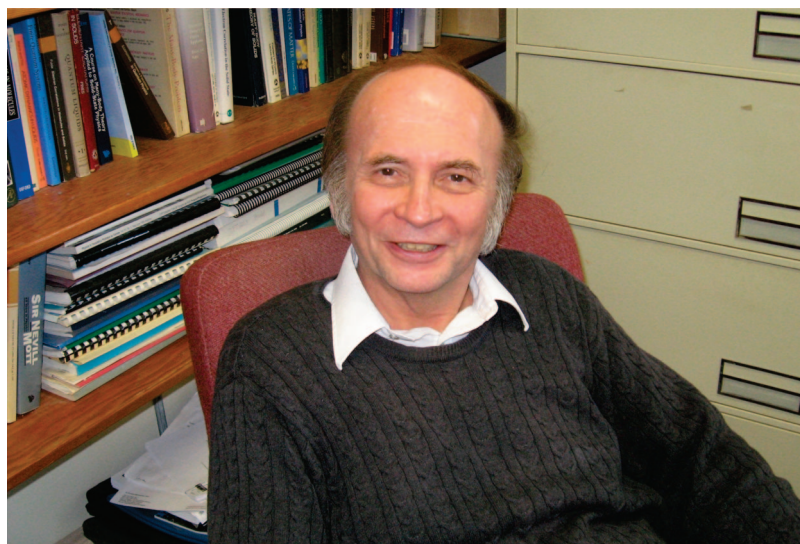


# JCTC

Journal of Chemical Theory and Computation

## Special Issue in Honor of John P. Perdew for His 65th Birthday



### Short Biography: From a Conversation with John Perdew

John Perdew was born August 30, 1943, in the Appalachian mountain region of western Maryland. He grew up in the small city of Cumberland, where his parents, Paul Perdew and Elma Carr Perdew, were both teachers. At Allegany High School, good mathematics courses convinced him that some things could be proved. A National Merit Scholarship brought him to Gettysburg College in Pennsylvania, where Professor Richard Mara's elegant introductory lectures left no doubt in John's mind that mathematical clarity and physical intuition could come together in one science: physics.

John was a graduate student of physics at Cornell 1965–1971, a turbulent time for many and a time of challenge for him—first to get through the graduate courses and then to find (over a period of several frustrating years) a successful approach to his dissertation problem. There his thesis advisor John Wilkins and his teachers Neil Ashcroft and David Mermin got him started on solid state theory. After the completion of his dissertation, he got his first taste of theoretical chemistry when Wilkins asked him to try to explain the cooperativity effect in the oxygenation of hemoglobin. But his freshman chemistry course had not prepared him to deal with such a large and complicated system.

At that time, electronic structure calculations for solids, when they were done at all, were still typically based on the Hartree approximation. Some physicists and chemists

were exploring the local density or Slater  $X\alpha$  approximations, but that information did not trickle down to John. The density functional theory of Kohn and Sham 1965 was first presented to him when he was a postdoc with Sy Vosko at Toronto 1971–1974. A second postdoc fellowship with David Langreth at Rutgers 1974–1977 convinced him that this theory was a sound foundation on which to build both improved approximations and successful applications.

The late 1970s were a hard time to find a job in physics. In his later postdoc years, John sent out hundreds of applications per year, usually without getting an interview. He even applied for an experimental faculty position at Tulane University in New Orleans and was hired there in 1977 (since experimentalists were too expensive!). John has spent more than 30 happy years there, exploring the exact density functional theory and constructing/testing its needed approximations, never tiring of this deep and practically important subject, enjoying the good company of more faculty colleagues, postdocs, and students than can be named here.

John's first collaboration with Mel Levy of Tulane Chemistry was "In Defense of the Hohenberg-Kohn Theorem and Density Functional Theory", *Int. J. Quantum Chem.* **1982**, 21, 511. This article was officially labeled a "polemic" in an editorial in the same issue. Kieron Burke, now at UC Irvine, Chemistry, joined his group as a postdoc in 1993.

My research collaboration with John commenced in August of 2002 after a Sandia Workshop in Albuquerque on density functionals. At the time, it was increasingly clear that *local* hybrids (or hyper-GGAs in John's "Jacob's Ladder" hierarchy of functionals) were the way forward. In Fall 2005, with Hurricane Katrina seriously devastating New Orleans, John spent a forced sabbatical in my group at Rice University in Houston. He endured the near miss of another big category 4 storm (Rita) that same Fall. Twenty-two papers and several functionals later, our joint scientific adventure still continues.

Gus Scuseria  
Rice University

## Early Days at Tulane

It gives me pleasure to recall the early days at Tulane, where I often interacted and collaborated with John.

I arrived at Tulane a year before John began his faculty appointment. Prophetically for DFT, Walter Kohn visited and reviewed the Physics Department during that year, thus anticipating (or perhaps causing) John's appearance. I first met John in 1977 at his job interview lecture, which took place in the planetarium, an appropriate venue in which to discuss the universal functional.

I came to Tulane with the intent of concentrating on DFT. Wonderful for me was the coincidence that John was hired. The odds were close to zero in those days that two people, in two relatively small departments, would work on the fundamentals of DFT and would happen to have offices about 50 feet apart on the same floor.

The semiofficial Quantum Theory Group was formed in 1977, composed of faculty members from physics, chemistry, and mathematics. For years we regularly held spirited informal seminars on our research. Members of the group attended John's lively and lucid DFT course during his first or second year at Tulane.

Driven by our addiction to the subject and also somewhat, perhaps, by the fact that we were junior faculty members, at odd times we were the only people working on the fifth floor of Stern Hall. Indeed, I remember this to be quite clearly the case 30 years ago, between the Fall and Spring semesters of the 1978–1979 academic year, when I walked a few steps to John's office to show him some observations that eventually resulted in my first real DFT publication at Tulane. He was always there to share the excitement and make insightful suggestions. He was also very generous with his ideas.

Several years after the famous Perdew–Zunger self-interaction correction paper [*Phys. Rev. B* **1981**, 23, 5048], John excitedly came to me and said that he arrived at something very promising, a real-space cutoff of the gradient expansion for the exchange hole [*Phys. Rev. Lett.* **1985**, 55, 1665]. He said the numbers looked really good. I quote: "They have to be, given the quality of the theory." The work corrected the divergence problem of the second-order gradient expansion approximation (GEA). A correlation energy paper followed closely [*Phys. Rev. B* **1986**, 33, 8822]. These two papers marked John's entrance into research on the

GGA, a term that I believe he coined. We now know the delightful consequences of all this.

John and I have, of course, published a number of articles together. After our collaboration on the "polemical" *Int. J. Quantum Chem.* paper, our next joint venture was the PPLB article containing surprising results concerning fractional particle number and derivative discontinuities of the energy [*Phys. Rev. Lett.* **1982**, 49, 1691]. My family spent part of the summer of 1982 in Newton, MA. It was then that drafts of the manuscript were transported between Tulane, Newton, and Chapel Hill, where Bob Parr was and still is located. John suggested that we use Federal Express: "Let's get it out fast." This was my first exposure to FedEx, and as a result I still feel excitement when I walk into one of their offices. Anyway, our band gap paper followed soon after [*Phys. Rev. Lett.* **1983**, 51, 1884]. In the mid 1980s we collaborated on our counterintuitive coordinate scaling results and virial theorems in DFT [*Phys. Rev. A* **1985**, 32, 2010]. It was, as usual, much fun.

In those early days, there was always a feeling of anticipation that something wonderful was eventually going to happen with DFT. There was this mysterious functional, and all one had to do was crack its code.

Mel Levy  
Guest Editor

Duke University (Visiting Professor)  
Tulane University (Professor Emeritus)

## On the Border

In September 1993, I arrived at Tulane as John's new postdoc. For condensed matter theory, times were even rougher than in the early 1970s. I had already been a postdoc for four years and looked headed for academia's dustbin. Although I had never worked in DFT, John took a big chance on hiring me, giving me an opportunity for which I will always be grateful.

John had one or two graduate students back then, but I was his first postdoc for a long time. He was toiling away at the (now standard) DFT-developer tasks: constructing new functionals, finding new exact conditions, explaining failures, publishing errata, etc. Because the group was small, he had time to meet me every day, usually for lunch and coffee afterward. Every day, I would ask really dumb questions, often for the third or fourth time. Every day, he would explain things to me, never running out of patience, and always appearing to enjoy it. After about 3 months, I kind of got my bearings, the questions improved, and the answers were fascinating.

Up to about that time, DFT was an obscure subject studied by a handful of devotees. Every year, there would be one DFT session at the APS March meeting, which would be standing room only. But that was because users were hoping for a new functional and usually left empty-handed. The DFT die-hards would go have supper together that night, often fitting around a single table, and talk endlessly about all their favorite DFT exotica. Funding was always scarce, and many had paid their own way to the meeting.

John had recently created a generalized gradient approximation (GGA) called PW91, but it was largely being

rejected by the unwashed masses of condensed matter physics. This was because that community had become so used to the local density approximation (LDA or S-VWN5) that most of their codes were constructed to function only at that level of accuracy. During the first APS meeting after I began with John, I could not move from one room to another without someone stopping me to explain why GGAs do not work.<sup>1</sup> Since my first project was to check and help publish the PW91 derivation, this career move did not look too promising.

Meanwhile, there was a revolution taking place in chemistry, because it had just been shown that GGAs and hybrids were sufficiently accurate for many chemical purposes, and suddenly real chemists (not just theoretical ones) were using DFT. Barriers were coming down between the two disciplines, and John was getting invited to lots of chemistry meetings. We were writing up more and more material. Because there was so much stored in John's brain and published in obscure manuscripts without figures, whenever we could simply figure out how to calculate something inside the theory for a model system, we would see new things in the figures we had made or find a new molecular context for the work. I recall that after Matthias Ernzerhof joined us, we submitted our first article to the *Journal of Chemical Physics*, which naturally was roundly rejected by the referees. (It was later accepted, once we had done a better job of explaining what we were trying to do and had taken most of the DFT out.)

As time went on, we wrote and published a lot. One of the most pleasurable aspects was our joint love of the English language, and our constant attempts to run jokes past the editors. In particular, John always loved coming up with catchy titles to the papers. One of our favorites, "GGAs: A Glance under the Hood", was rejected by an ACS publisher, because chemists searching abstracts would assume we were working on fume hoods. We also fought a losing battle against acronyms (at least, those not beginning with a P).

Our most well-known work from that period was the GGA called PBE. This was really the triumphant culmination of two decades of John's work on GGAs but was also catalyzed by several key events. One was the refusal of *Physical Review B* to publish the complete derivation of PW91, on the basis that some of the material had already appeared.<sup>2</sup> Another was my observation that, when parametrizing the results of the numerical construction of the GGA exchange-correlation hole into the PW91 energy density, John had accidentally (and ever so slightly) screwed up an exact condition. That really stuck in his craw. The last I will mention is that, in order to satisfy as many constraints as possible, John had inserted some very small terms that do not kick-in except at very small gradients, ensuring restoration of the original gradient expansion. This would sometimes lead to nasty wiggles in the potential, unnecessarily raising lots of cut-offs in plane-wave codes.

Thus, John was inspired to produce a final GGA that would contain only those elements needed for calculations, and that could be explained by relatively transparent physical arguments. In fact, PBE is very similar to PW91,

but somehow it was the right functional at the right time for condensed matter physics.<sup>3</sup> Weitao Yang was the first in a long line to revise PBE, so we enjoyed pointing out his Procrustean dilemma. A quick second was the Danish RPBE of Hammer and Norskov, who asked the important question, PBE or not PBE. This was followed by so many more that John himself finally got into the game with the balefully named PBEsol.

At my last APS meeting as John's postdoc, I had the pleasure of watching Don Hamann<sup>2</sup> explain to a huge audience on a huge screen that PBE was giving the right answer for the right reasons for a pressure-induced phase transition in quartz, and I never had to defend PBE to physicists again. Thus, given its motivations, PBE is really just one more John Perdew erratum, correcting a few last functional typos in PW91 and pulling one more fast one on the editors of *Physical Review Letters*.

In all, I spent 3 years at Tulane, and those were the most research-productive years of my life. John and I wrote over 30 papers in that time, with many great collaborators. These years were also the most fun, because John made them so, with his relaxed informal approach to everything and his allowance for independence.<sup>4</sup> Not only did I learn all I needed about DFT to make a career from it, I also learned vital skills for writing papers, explaining ideas, and surviving in academia. These served me well in finally getting a faculty position at a small (but wonderful) chemistry department, something I never managed to do in physics, and a step I have never regretted.

A few years later, I was happy to return to Tulane for a mini-meeting with John and Mel and Hardly Gross, just 2 weeks after Walter Kohn shared a Nobel Prize in Chemistry.<sup>5</sup> We were all very happy but had no idea just how big, broad, and exciting the field would subsequently become. Much of the physics underlying that award came from the exceptionally deep and patient work of John, so his work truly lies on the border between chemistry and physics.

I am very happy to have helped contribute to both John's scientific enterprise as well as to this special celebratory issue. We on the border salute you, John, and look forward to many more functionals and fun article titles.

Kieron Burke

Guest Editor

University of California, Irvine

## References

- (1) There are still a few die-hards in condensed matter that prefer LDA, which gets the lattice constant of bulk silicon almost exactly right. Even PBEsol did not beat that.
- (2) Don Hamann is an extremely distinguished solid-state theorist who spent much of his career at Bell Labs. He mentioned that it took him 2 weeks of hard work in the library at the Aspen Center for Physics to find and read all the bits of the PW91 derivation, scattered as they were over many papers and years. In summer 2001, he also pointed out to us that PBE gets the ground-state energy of the hydrogen atom right to about 4 digits and wondered if we had done some surreptitious fitting. This was news to us

and either just dumb luck or some fundamental consistency in the universe.

- (3) Of course all good chemists know that PBE is woefully inadequate for many dissociation energies and that you really need a hybrid, such as PBE0, a.k.a. PBE1PBE.
- (4) Another bonus that came with being at Tulane was the chance to interact and collaborate with Mel Levy who was in the chemistry department. He famously wrote in his research proposal when he applied for a faculty position there that he would find the exact XC functional (which, in a sense, he did

with his constrained search approach). This was a brilliant move, as he spent his entire career at Tulane working on that original proposal, and he is still not finished!

- (5) This was when Hardy Gross (a.k.a. E.K.U.) first asked me about how to calculate conductances through single molecules, a project he and I have happily worked away at for a decade now. Hmm, sounds quite like Mel's original proposal.

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