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The rocky path of DFT into chemistry—Discussions at a symposium and reflections on a circular journey in honor of Axel Becke 1953–2025

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The rocky path of DFT into chemistry—Discussions at a symposium and reflections on a circular journey in honor of Axel Becke 1953–2025

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ABSTRACT

We summarize a recent symposium on density functional theory for electronic structure in chemical applications and honor a key contributor, Axel Becke. The theory of electronic structure is entirely quantum mechanical and, in its original wave function form, runs into mathematical and numerical problems due to high spatial dimensionality, as each electron adds three new coordinates. The approximate reduction of dimensionality in the form of density functional theory (DFT) was first proposed in the mid-1920s but took 40 years to be verified as possible in principle. The development of increasingly accurate functionals, expressing the electronic energy in terms of the density of the electrons, was initially driven by the physics community, but after a series of innovations, including (i) going from local to non-local exchange–correlation energy functionals and (ii) partial retention of exact exchange in terms of wave functions, there was a breakthrough in the early 1990s, and leading quantum chemists accepted DFT. The resulting improved ability to solve chemical problems by computation was rewarded with a Nobel Prize to Walter Kohn and John Pople in 1998. Given the many controversies surrounding the introduction of DFT into chemistry, a symposium was held at the Royal Swedish Academy of Sciences on November 7 and 8, 2024, to look back at the barriers and breakthroughs

and identify the key contributors and their advancements. Axel Becke played a major role in bringing DFT into chemistry. We record the unique breadth and depth of the discussions at the symposium and the role of Becke, whose life ended a year thereafter.

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Introduction

The method of density functional theory (DFT) has reshaped the study of chemistry by computational theory in the last half century. In particular, the electronic structure of atoms, molecules, and materials is now accessible to computation mainly by DFT, which has complemented the original wave function form of "quantum chemistry" and allowed much larger systems with hundreds of atoms to be studied. A Nobel Prize was awarded in chemistry to Walter Kohn and John Pople in 1998, mainly for the original conception of DFT in modern form (Kohn 1964–1965) and for contributions to quantum chemistry, including the introduction of DFT to chemists in the early 1990s (Pople). Between these occasions, electronic DFT went through a period of development that included meeting and overcoming serious objections, particularly from the community of quantum chemists. This "rocky path" was the subject of a symposium held at the premises of the Royal Swedish Academy of Sciences on November 7 and 8, 2024. The symposium had the title "DFT in Chemistry—Dispute at Inception and Rise to Prominence" with the specific purpose of examining and helping resolve any remaining issues that hindered DFT in its path to current prominence in chemistry and of looking to the future. What follows below is a recollection of this discussion in honor of a key contributor, Axel Becke, who, one year after the event (October 23, 2025), has left us to carry on in his indomitable spirit.

The summary of the discussions at the symposium is based on the abstracts of the talks that were edited a year later by the speaker. A few contributions from people close to DFT and Axel Becke have been added. Bridging comments and reflections are offered by the first author acting as an editor. The talks at the Royal Swedish Academy of Sciences were recorded and are accessible for further study.

How the Search for a Simpler Form of Quantum Mechanics Produced DFT—Some Basic Facts

Quantum mechanics, now recognized as the foundation of chemistry, was developed first in the form of matrix mechanics by Heisenberg,[1] and within a year, in the form of wave mechanics by Schrödinger.[2] It was found difficult to grasp and implement computationally. Thomas and Fermi soon[3,4] independently proposed that, for studies of electronic structure, quantum mechanics could be formulated approximately in terms of "electron density only" in order to achieve great simplification of both physical interpretation and calculation. Nevertheless, the wave function form of quantum mechanics, as conceived by Schrödinger, remained dominant in its joint field of physics and chemistry for about 60 years. The Thomas–Fermi theory, the original form of DFT (density functional theory), remained an important option but was rarely used and received a severe setback from the point of view of chemists when Teller[5] showed that it could not resolve covalent bonding in molecules. This was certainly a major "rock in the road" for DFT, but few chemists were aware of it.

It seemed as if DFT was not a viable option for electronic structure until Hohenberg and Kohn, in 1964,[6] showed that, in principle, it was possible to determine ground state electronic structures by "density only analysis" but provided no practical way of doing so. The following year, Kohn and Sham[7] formulated modern DFT (often denoted KS-DFT) by suggesting that the electron density be composed of one-electron orbital contributions and the kinetic energy be evaluated by wave function quantum mechanics with the electrons moving independently as described by these orbitals. This Kohn–Sham model employed wave functions in contradiction to the Hohenberg–Kohn proof that they were not needed "in principle." The reintroduction of wave functions (in the form of one-electron orbitals) to violate the original premise of "density only" is certainly another "rock in the road" of DFT. Many quantum chemists will have felt justified in sticking with the full wave function theory, while some of them, and most physicists in the field, were pragmatic and interested in exploring the great simplifications that KS-DFT still offered.

Within the physics community, after 1965, the development of forms of what we could call KS-DFT continued, which provided increasingly accurate results for solid systems. Interestingly, the naming of the methods by the acronyms DFT or KS-DFT took some years to settle in preference to "inhomogeneous electron gas," "Hartree–Fock–Slater," and other names relating more to "approximate Hartree–Fock" than to the new DFT of Hohenberg–Kohn–Sham.

Chemists, who had developed "*ab initio* quantum chemistry" based on wave functions in finite basis set expansions, were in the 1970s and 1980s reluctant to abandon their reliable, if demanding, methods to instead take up unreliable, but simple, DFT methods. Physicists who attempted to explore chemistry by early forms of DFT were often met with skepticism, if not outright hostility. The latter was often provoked by the Xα-method, which used a parameterized and greatly simplified treatment of exchange in terms of local electron density. This method was originally proposed by Slater already in 1951,[8] well before the foundation of modern DFT was laid in the mid-1960s. Studies that oversold the merits of Xα-calculations for molecules, sometimes performed without the needed computational accuracy, appeared in the 1970s and deterred many "*ab initio* quantum chemists" at the time. A major "rock in the road to quantum chemistry" of DFT bore the name Xα, but not all quantum chemists were deterred. Physicists studying condensed matter were naturally more open to simplifying approximations in view of the essentially infinite number of electrons in their systems.

This is where our symposium discussions start. They look back at disputes about quantum mechanics implemented "*ab initio*" in terms of wave functions or, alternatively, in terms of electron

density. These disputes slowed progress but were eventually resolved to allow DFT into chemistry. The passage of the barriers mentioned (the "rocks in the road") opened the doors to a new era of electronic structure computation for a much-expanded range of systems and problems, while leaving some fundamental problems still unresolved.

Axel Becke was certainly a key contributor to the successful entry of DFT into chemistry. The recollections and reflections of the expert contributors below will make that clear. However, he was himself also well aware of the remaining limitations of even his favorite forms of DFT. He ended a brilliant talk on seminal contributions with an admission that he was a bit lost as to where to take his DFT functionals next. We will have to hope that his outstanding example will inspire others to continue his uniquely insightful work into new productive directions.

Abstracts of Talks (with revisions) at the Symposium "DFT in Chemistry—Dispute at Inception and Rise to Prominence," Stockholm, November 7 and 8, 2024.

Evert Jan Baerends, Vrije Universiteit, Amsterdam, The Netherlands (Revised December 2025)

From Xα to DFT to DMFT—An XC Hole Perspective

Early days: The black sheep. In 1981, I gave a talk at McMaster University on the subject of Xα (also called Hartree–Fock–Slater, HFS) calculations. I vividly remember the piercing dark eyes of the graduate student who came to me after my talk, telling me he felt it was worthwhile to concentrate on numerically solving the Hartree–Fock–Slater equations. This was at a time when Xα (or LDA) was thoroughly unpopular in the quantum chemistry community. The student was Axel Becke. We remained in touch, partly through Ziegler in Calgary, but I had no premonition of the important role Axel was going to play in the development of DFT.

It is a question for historians of science to clarify why exactly in the seventies and eighties HFS/Xα was so unpopular, the black sheep of the quantum chemistry community. The scattered wave method had rattled this community with its claims of orders of magnitude faster electronic structure calculations.[9] Claims of more accurate results than Hartree–Fock could be dismissed on account of the muffin-tin approximation, which was evidently too severe for elementary molecular properties such as geometries. However, solving the Xα or LDA one-electron equations can be done with the standard basis set expansion (LCAO) method.[10] This is definitely slower than the scattered wave technique. However, when the electronic energy and potentials—Coulomb and exchange–correlation—are only density (-gradient) dependent, it is possible to do away completely with the calculation and processing of two-electron repulsion integrals (ERIs), using density fitting and 3D numerical integration. The ERIs (N^4-scaling) were at the time the main cause of the high computational demand of Hartree–Fock calculations, limiting their applicability to small systems, at most, simple transition metal systems. The LCAO-HFS/Xα calculations (N^3-scaling due to the density fitting) were much faster, bringing a much wider range of chemistry within reach. Even within the limited numerical precision that was initially possible, the HFS model clearly proved to be more accurate than Hartree–Fock for several properties,[11–14] and notably for transition metal complexes.[15–18] There were suspicions that the computational methods were not reliable, and therefore the claim that the underlying electronic structure model substantially improved upon the Hartree–Fock model would be unwarranted. The numerical precision, even if limited for some properties in the seventies, was definitely sufficient to make the interesting difference with the HF model clear. Precision, also for bond energies, was certainly not a problem anymore by 1980.[17–20] However, it was the speed of the computations that propelled the HFS/Xα method through the seventies and eighties. The good quality of the results—sufficient for many chemical problems—does not seem to have been a major factor in the appreciation, causing, in the *ab initio* community, maybe more irritation than admiration. *Ab initio* quantum chemistry concentrated massively, and more systematically, on methods better than Hartree–Fock (i.e., correlation energy) anyway.

HFS/Xα has been applied through the eighties for organometallic chemistry, clusters, transition metal complexes, and heavy elements (relativistic effects); in short, in cases where *ab initio* quantum chemistry was out of its depth because of huge computational burden. It is now generally accepted that density fitting and 3D numerical integration, when applied carefully, can perform quite reliably. They have been applied in Gaussian function based codes by Dunlap, Rösch, Salahub, and co-workers and have now been incorporated in all major quantum chemistry codes. Density fitting, in various forms, has even emerged as an important tool to speed up many types of "*ab initio*" calculations (Hartree–Fock, MP2, and coupled cluster). Axel Becke published, true to his promise, in 1981, an alternative, fully numerical method (initially for diatomics, later generalized to arbitrary molecules) that allowed basis set free results to be obtained. He established the numerical precision of his method on dissociation energies to be better than 0.1 eV (2.3 kcal/mol) in his 1982 paper.[21] This has certainly helped to give his later results the reputation of incontestability.

The turning point. After some other attempts, Becke published in 1988 a paper in which he proposed a correction term to the LDA exchange energy (which is virtually the same as the Slater exchange). He showed it approximates the Hartree–Fock exchange energies of the rare gas atoms (and later of a larger sample of atoms) to better than 0.01 au (6 kcal/mol).[22] This led up to his epochal 1992 paper,[23] where he showed that in combination with the LDA (homogeneous electron gas) correlation functional, the average absolute error of the heats of atomization of a large sample of molecules was reduced from 36.2 kcal/mol for LDA to 3.7 kcal/mol (0.006 a.u.) (surprisingly even better than the roughly 6 kcal/mol accuracy of the B88 exchange for atoms). The psychological effect of this work can hardly be overestimated. It convinced leaders in the *ab initio* community such as John Pople that the promise of DFT might come true: it proved to be possible to find simple density (and density-gradient) dependent exchange–correlation expressions that would give reliable "correlated" energies. Given the computational expediency of DFT calculations, this was something of tremendous practical importance. Many quantum chemists followed Pople's lead in adopting this new paradigm. The exchange approximation developed earlier by Perdew (see Ref. 24 and references therein) has a similar beneficial effect for dissociation energies. Becke's adoption of Pople's construction of a model chemistry consisting of a well-performing computational strategy for a benchmark set of

molecules (Becke used the 55 molecules of the G2 set) was instrumental in convincing Pople and the rest of the *ab initio* community.

Of course, questions remain. Becke's 1988 exchange approximation is devised as a good approximation for the exact Hartree–Fock exchange energy. The LDA+B88 approximation (B88 for short) was indeed shown to be accurate for atoms[22] at the mentioned ~0.01 Hartree (6.3 kcal/mol) level. For heats of atomization (dissociation energies), Becke retained in Ref. 23 the LDA correlation energy, commenting that this has such a small effect that improvements can be neglected in a first approximation. However, then one might, with a good exchange approximation, naively expect dissociation energies to become exact-exchange (Hartree–Fock) like. That would imply that the bond energy reverts from the moderate overbinding of LDA to the severe underbinding of Hartree–Fock. However, the eye-catching result was the avoidance of either underbinding or overbinding. One can probe these energies a bit deeper by comparing them to exact exchange and correlation energies for prototype molecules such as H_2, Li_2, N_2, and F_2; see Table I (numerical results from Ref. 25). "Exact" means for the determinantal wave function with the exact Kohn–Sham orbitals. The exact exchange energy is defined with the exact Kohn–Sham orbitals, and the correlation energy is defined as the difference between the exact and KS determinantal energies. The "exact" KS orbitals are generated from a very accurate electron density, obtained with MRCI calculations, using the so-called inverse KS method of obtaining the KS potential corresponding to the density. The method proposed in Ref. 27 has been used. It is basically an iterative application of the Hohenberg–Kohn relation $\int \Delta v(\boldsymbol{r})\Delta\rho(\boldsymbol{r})d\boldsymbol{r} < 0$ (see also, e.g., Refs. 28 and 29): when locally the density generated with a trial KS potential differs by $\Delta\rho(\boldsymbol{r})$ from the exact target density, the potential differs from the exact potential by a local $\Delta v(\boldsymbol{r})$ of opposite sign to $\Delta\rho(\boldsymbol{r})$. The KS potential has to be updated accordingly in order to get a better density.

The exchange energies turn out to be very close for exact KS and Hartree–Fock determinants.[25] This is in spite of the HF density and the KS (equal to exact) density differing markedly, with large concomitant differences in Coulomb energy terms (electron–nuclear as well as electron–electron) and kinetic energies. Table I (upper half) demonstrates the well-known fact that the LDA exchange energies are (very roughly) some 10% in error (not negative enough) for both molecules and atoms. We note that indeed the B88 correction leads to a spectacular reduction in the large LDA error for atomic exchange energies; see the upper right panel of Table I. This success is not repeated for the molecular exchange energies; see the upper left panel of Table I, although the B88 correction does improve considerably on the LDA exchange energies. Actually, the B88 correction tends to overshoot, making the exchange energies somewhat too negative. Interestingly, the B88 exchange energy proves to be a closer approximation, in molecules, to the *sum* of the exact exchange energy plus the near-degeneracy (or left-right) correlation energy (see Ref. 25 for this comparison and the definition of the left-right correlation). This gives some credibility to the old notion that the exchange approximations that work with localized holes, as the Slater/LDA exchange approximation does, implicitly also model the left–right correlation in chemical bonds, whose omission in the Hartree–Fock model is the main cause of the very poor bond energies obtained with that model. However, the agreement is not quantitative; discrepancies are often in the 0.02 au (12 kcal/mol) range and for F_2, even 0.087 au (54 kcal/mol),[25] far beyond the 3.7 kcal/mol achieved by Becke in Ref. 23. Of course, an approximate exchange expression that is fitted to atomic exchange energies is not designed to contain left–right correlation.

Regardless of such reinterpretation of the exchange part of a functional for the exchange–correlation energy, which also requires a reinterpretation of the correlation part, we can try to analyze the basis for the success of the B88 exchange plus LDA correlation strategy for the dissociation energies numerically. We compare in Table II the exact total exchange–correlation energies (left panel) with the B88 exchange plus LDA correlation (right panel). Subtracting the exchange–correlation energies for the atoms, the exchange–correlation contribution to the dissociation energy is obtained in the two cases {the dissociation energy is defined as the negative number $[E(\text{molecule}) - \sum E(\text{atom})]$}. It is clear that the B88/LDA exchange–correlation contribution differs considerably from the exact one, rather more than the excellent 0.006 a.u. (3.7 kcal/mol) that was achieved on average for the total dissociation energy with the B88/LDA procedure. The implication is that the other energy contributions to the dissociation energy—kinetic energy and electron–electron and electron–nuclear potential energy differences between molecules and atoms—are different in the exact and B88/LDA cases in such a way that they compensate for the error of the B88/LDA exchange–correlation energy. (Becke used LDA SCF orbitals, so these energy terms were the LDA ones in his work.)

Why does this happy cancellation of errors occur between, on the one hand, the contributions of the Becke88 exchange energy plus LDA correlation energy to the bond energy and, on the other hand, the LDA approximations of the other energy terms? We do not know. It appears almost intractable to find any physics that would be responsible for this phenomenon. It certainly is not happening by design.

I remember vividly raising with Axel my concerns about the less than clear physics that is behind this and many other proposals for new functionalities. Axel did not share my feeling. He thought that these were typical "Old World" considerations (maybe a polite way of saying "old-fashioned" or "outdated"). According to Axel, in the New World (maybe he meant in modern times), it is vastly more important that things work than to understand why they work. One might say that the impact of his work has proven him right.

The XC hole. Where are we heading? It is unfortunate that the Hohenberg–Kohn theorem, although establishing the unique mapping between energy and density, does not give a clue as to how to find a relationship. It might be that two densities that are close by some distance measure between functions in the applicable function space may still correspond to a large energy difference. In other words, there is no route given toward analytical expressions for a density–energy relation. The existence of such an analytical relation is actually unlikely. We can take the central issue of left–right correlation as an example. When in the electron-pair bond between atoms A and B, one electron is on atom A, the other is more likely to be on B, at elongated bonds very much so. This is described by the conditional probability $\rho^{\text{cond}}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ of finding another electron at a position $\boldsymbol{r}_2$ when a given electron is at $\boldsymbol{r}_1$. However, the density at a position $\boldsymbol{r}_1$ at atom A, or its gradient, etc., does not tell

TABLE I. Exchange energies (upper panels) and correlation energies (lower panels). Molecular quantities (exact, LDA, B88, and Perdew–Wang[24]) are from Ref. 25. The orbitals used for the exact exchange and correlation energies (difference of KS determinantal energy and exact energy) are very accurate ("exact") Kohn–Sham orbitals. Molecular B88, LDA, and PW exchange energies have been calculated from the corresponding Kohn–Sham (=exact) density. Atomic exchange energies are from Ref. 22, and atomic correlation energies (exact and LDA) are from Ref. 26.

Diatomic molecules				
		Exchange energies		
	Bond energy	Exact mol. exch. energy	LDA mol. exch. energy	B88 mol. exch. energy
Li_2	0.039	−3.565	−3.084(+0.481)[a]	−3.555(+0.010)[a]
N_2	0.364	−13.114	−11.873(+1.241)	−13.208(−0.094)
F_2	0.062	−19.935	−18.211(+1.724)	−20.101(−0.166)
H_2	0.174	−0.661	−0.569(+0.092)	−0.658(+0.003)
		Correlation energies		
	Bond energy	Exact mol. correl. energy	LDA mol. correl. energy	Perdew–Wang mol. correl. energy
Li_2	0.039	−0.128	−0.330(−0.202)[a]	−0.137(−0.009)[a]
N_2	0.364	−0.552	−0.942(−0.390)	−0.490(+0.062)
F_2	0.062	−0.755	−1.296(−0.541)	−0.669(+0.086)
H_2	0.174	−0.039	−0.095(−0.056)	−0.046(−0.007)
Atoms (double)				
		Exchange energies		
		Exact 2^* at. exch. energy	LDA 2^* at. exch. energy	B88 2^* at. exch. energy
2 Li		−3.562	−3.076(+0.486)[a]	−3.550(+0.012)[a]
2 N		−13.192	−11.786(+1.406)	−13.178(+0.014)
2 F		−20.00	−18.104(+1.896)	−20.04(−0.04)
2 H		−0.626	−0.536(+0.09)	−0.620(+0.006)
		Correlation energies		
		Exact 2^* at. correl. energy	LDA 2^* at. correl. energy	
2 Li		−0.090	−0.302(−0.212)[a]	
2 N		−0.372	−0.860(−0.488)	
2 F		−0.632	−1.288(−0.656)	
2 H		−0.000	−0.044(−0.044)	

[a]Difference with exact between parentheses.

where atom B is located. That location is, of course, crucial for the energy. In order to bring in this essential information, one needs the orbitals, as is evident from the prototypical configuration interaction between the $(\sigma_g)^2$ and $(\sigma_u)^2$ configurations in dissociating H_2. An exact functional for dissociating H_2 can be formulated by expressing the conditional density by way of the exchange–correlation hole using the σ_g and σ_u Kohn–Sham orbitals.[30,31] A consistent development seems to be that we find reliable and accurate models of the exchange–correlation holes belonging to specific correlation cases. That is not straightforward. The problem is aggravated by the requirement that, in the Kohn–Sham orbital method, the relevant hole is not the "simple" hole that describes the conditional probability. The complication arises from the Kohn–Sham kinetic energy T_c, the difference $T_c = T - T_s$ between the exact kinetic energy T and the one from the Kohn–Sham orbitals, T_s. T_c has to be built into the Kohn–Sham exchange–correlation energy E_{xc}. For this, we need the holes for any coupling constant λ in systems with electron interaction λ/r_{12}. It might be simpler to start with density *matrix* functional theory (DMFT), where only the simple conditional density $\rho^{\mathrm{cond}}(\boldsymbol{r}_1, \boldsymbol{r}_2)$, without coupling constant integration, needs to be modeled. In that case, the kinetic energy is directly given by the one-particle density matrix. It is the increasingly more accurate modeling of the exchange–correlation hole, either in its pure form in DMFT or in the coupling constant integrated form in DFT, for the whole variety of correlation cases that occur in chemistry, that is the equivalent of the ever more accurate modeling of the wave

TABLE II. Left: exact total exchange plus correlation energies (xc energies, second column) for the listed molecules and the difference with twice the exact atomic xc energies (third column), which is the exact xc contribution to the dissociation energy. Right: total molecular xc energies from B88 exchange plus LDA correlation energies (fourth column) and the differences with the atomic B88+LDA xc energies (fifth column), which is the B88+LDA xc contribution to the B88+LDA dissociation energy.

	Exact exch.–correl. energies		B88+LDA exch.–correl. energies	
	Molecular xc energy	Difference with 2*atomic (xc contrib. to dissociation energy)	Molecular xc energy	Difference with 2*atomic (xc contrib. to dissociation energy)
Li_2	−3.693	−0.041	−3.885	−0.033
N_2	−13.666	−0.102	−14.150	−0.112
F_2	−20.690	−0.058	−21.397	−0.069
H_2	−0.700	−0.074	−0.753	−0.089

function by increasingly more sophisticated configuration interaction strategies in wave function theory. For now, many attempts in DFT are still guided by a mixture of physical reasoning and intuition, for which success is not guaranteed. It is a sobering thought indeed that we have not progressed very much beyond the level that was achieved around 1990 by the work of Axel Becke and John Perdew.

Axel Becke, Dalhousie University, Canada † October 23, 2025

Full Circle—My Life in DFT

The roots of my interest in DFT go way back to the late 1970s and the Hartree–Fock–Slater, or "Xα," local exchange model. I was fascinated by how easily this model would predict molecular bond energies compared to the existing WFT (wave function theory) methods such as Hartree–Fock, MP2 (Möller–Plesset second order perturbation theory), etc. Its accuracy, however, was insufficient for routine chemical purposes. I discovered through the 1980s that simple corrections involving density gradients could improve things enormously. At the International Conference on Quantum Chemistry, Menton, France, in 1991, I presented an assessment of our latest gradient-corrected DFT bond energies on the 55 molecules of the G1 thermochemical test set of Pople and co-workers. The results were compelling enough that Gill, Johnson, Pople, and Frisch released Gaussian 92/DFT featuring the "BLYP" functional soon thereafter. This was the turning point for DFT.

Many advances followed ... "hybridization" with Hartree–Fock, other variables beyond the density gradient, DFT models of static correlation and dispersion, and even "double hybridization" with MP2.

This talk will recount stories of my personal journey and highlights. I may even offer my opinion of where DFT/WFT stands today.

Kieron Burke, University of California, Irvine, USA
(Revised April 2026)

Density Functional Theory in Chemistry and Materials: From the Past to the Future with Machine Learning

I was one of Walter Kohn's last graduate students and one of John Perdew's first postdocs (in modern times). I will outline, based on memories and hearsay, the rise of DFT to prominence and practicality, starting in 1926. I will focus on the difficulties of acceptance within the quantum chemical community and the sea change that occurred between 1993 and 1998. As these events happily coincided with my own early academic career, but involved many of my distinguished colleagues, my view was definitely from the bottom.

In the second part of my talk, I will look to the future. I will argue that this year's (last month's, 2024) Nobel Prizes in physics and chemistry presage a revolution in materials science and chemistry, combining machine learning and DFT calculations. I will outline my vision of how we can finally realize the dream of (effectively) solving the Schrödinger equation for macroscopic pieces of matter.

On the passing of Axel Becke: Axel was a great contributor to the development of accurate approximations in DFT and played a key role in the revolution that led to the 1998 Nobel Prize in chemistry. We enjoyed many technical conversations together on the many occasions we met at conferences (we first met at Indiana University, just before I began my first postdoc with John Perdew in 1993). In 2011, I invited Axel to give an after-dinner talk at a meeting I co-organized in Dublin. He explained there that his greatest influence and source of inspiration was Slater and his four volumes, and this shows in his approach to DFT. Axel combined an appreciation for fundamental theory with tremendous insight and a pragmatic approach.

Although some folks equate Axel with the introduction of empirical parameters, in fact, Axel was proud of the fact that he introduced very few, that they were always physically motivated, and that it was quicker to fit them than to try to derive them. I provided a perfect example of this when, in 2009, with a graduate student, Peter Elliott, we were able to "derive" the one parameter in the B88 exchange functional, a mere 21 years after Axel published it. In his honor, we published in the Canadian Journal of Chemistry.

Much later, thanks to Erin Johnson, I was fortunate enough to be present for Axel's last public lecture at a meeting in Halifax, where he explained his latest functional and the reasoning behind it. I also

greatly enjoyed our last conversation over lunch one day. While he was energetic as ever, he did feel that, apart from some tidying up, he had essentially completed all his ideas about DFT.

I was a great fan of both Axel and his work. Time and again, covering many different aspects of DFT in chemistry, he published new and insightful ideas, combined with pragmatic molecular tests. With his passing, the field has lost a giant. I sorely miss him.

Peter Gill, University of Sydney, Australia (Revised January 2026)

John Pople's DFT Journey: From Skeptic to Enthusiast and Back Again

In the late 1980s, Pople and his collaborators introduced the general-purpose Gn models[32,33] for calculating accurate molecular energies. These were well received, but John was disturbed by Axel Becke's claims that DFT calculations using the generalized gradient approximation were almost as accurate and computationally very much cheaper. He suspected that skullduggery was involved, and we decided to attempt to reproduce Axel's results in a hacked version of the Gaussian software package. To our surprise, we discovered that Axel's results were legitimate, and we immediately initiated a comprehensive coding project within Gaussian to enable it to perform efficient DFT energy and gradient calculations and to pursue the development of functionals that were even better than Axel's.[34–38]

Our sudden change in research direction was noted in Cambridge (the Handy group), Houston (the Scuseria group), and elsewhere, and, in a few months, there was a sudden uptick in DFT-related publications, conferences, and workshops around the world. During this exciting period, Axel (in Kingston) and I (in Pittsburgh) chatted by phone every week or so, each eager to find out what the other was working on, while giving away as little as possible about his own research directions! I was remarkably fortunate to have been the postdoc in John's group at this time, soaking up as much as I could from the dazzling talent north of the border and the relentless discipline of my ultra-methodical mentor.

In early 1992, we sent a preprint to Axel of a paper[38] that investigated a hybrid of Hartree–Fock and density functional theories. Eq. (9) in that paper defines the extent to which Axel's famous 1988 exchange functional overestimates the true Fock exchange, a quantity that we had wryly designated the "Becke excess." Not long afterward, we heard Axel present an approach that was later recognized as the birth of Rung 4 functionals, and although he initially described his model as a "mixing," it has since been known as a "hybrid." Seeing the close relationship between the ideas in our preprint and Axel's new paradigm, John was annoyed with himself (and me). "We should have thought of that!" he said.

In the years that followed, John's enthusiasm diminished, and, by the mid-1990s, he had declared himself a "DFT skeptic." He felt confident that, notwithstanding the Hohenberg–Kohn theorem's siren call, it will always be extremely difficult to extract subtle, high-order correlation effects from the electron density alone, and he therefore concluded that, if one's goal is accurate molecular energies, the winsome simplicity of DFT's one-electron foundation is also its irredeemable weakness. He correctly foresaw that semi-empirical parameterization would increasingly dominate the development of new functionals, and, reluctant to return to a methodological framework that he had dominated in the 1960s, his interests turned elsewhere.

John died in 2004, and for the following 20 years, Axel (and numerous others) continued to pursue ever better functionals. However, the breakthroughs that had flowed so freely in the late 20th century proved much more elusive in the 21st, and, with the benefit of hindsight, it is probably fair to conclude that John's skepticism was justified. DFT has been an astonishingly successful computational tool, but one feels that we may have reached the fin de siècle. What lies ahead? It is difficult to say. However, without a doubt, we will need leaders such as John Pople and Axel Becke to guide us there.

Paola Gori-Giorgi, AI for Science, Microsoft Research (Revised January 2026)

From Academia to Microsoft Research: My DFT Journey

I spent more than twenty years in academia, where the central focus of my research was the improvement of the accuracy of density functional theory (DFT) through what was, at the time, a novel connection with the field of optimal transport.[39] I was extraordinarily fortunate to work with outstanding students and postdoctoral researchers, and I benefited immensely from exceptional supervisors and mentors: John Perdew, Andreas Savin, and Evert Jan Baerends. Unsurprisingly, many of Axel Becke's pioneering papers were a constant topic of discussion throughout my career. The depth, originality, and lasting impact of Axel's work were always mind-blowing. I also had the pleasure of meeting Axel in person at many conferences, where our discussions were invariably fascinating and deeply inspiring.

In 2022, I transitioned to Microsoft Research to pursue a highly ambitious goal: to use modern deep learning (DL) approaches to learn the exchange–correlation functional directly from high accuracy wave function data, together with an exceptional team of leading machine learning and quantum chemistry experts. The core idea is to provide the DL model with only semi-local information and to allow it to learn the relevant nonlocal features from data, thereby entirely bypassing the traditional cost–accuracy trade-off embodied in Jacob's ladder. Because representation learning is intrinsically data hungry, a crucial first step is the ability to generate large volumes of reliable, high-quality wave function data.[40] A first proof point of the viability of this approach is the initial release of the DL functional *Skala*, which achieves accuracy competitive with the best range separated hybrid functionals for main group thermochemistry while retaining semi-local computational cost.[41,42] *Skala* was trained on a first batch of 150k high-accuracy energy differences and continues to improve as additional data are incorporated during training, with forthcoming versions becoming increasingly accurate across a broader chemical space.

As progress accelerates through the synergy of deep learning and high accuracy wave function data at scale, it becomes ever more apparent how profoundly our work builds upon the foundations laid by giants in the field—chief among them Axel Becke. One need only count how frequently the name "Becke"

arises in our team meetings to appreciate this influence: the Becke integration grid and the B3LYP functional are the most frequent references, but countless other concepts and ideas from his work emerge time and again. I can only conclude with a deep sense of gratitude for everything Axel enabled through his original thinking and passion for science—along with great excitement for what lies ahead.

Stefan Grimme, University of Bonn, Germany (Revised November 2025)

Density Functional Theory: The Natural Choice for Large Systems and Non-Experts

Kohn–Sham density functional theory has become the practical default for studying large molecular systems. It offers manageable $O(N^3)$ scaling in many real cases and usually behaves in a stable, black box, fashion that appeals to non-experts. This position would not exist without the foundational work of Axel Becke. His contributions to exchange functionals, the idea of hybrids, and practical formulations shaped what many of us now treat as standard. Much of the routine reliability that users expect from KS-DFT traces back to ideas he introduced or clarified.

These strengths are real. They also come with limits. KS-DFT has long struggled with long range correlation (London dispersion), which leads to systematic errors in non-covalent interactions. For very large systems, the cost remains high enough to slow down high-throughput workflows. Axel Becke was well aware of such issues and took a sober view of the gap between formal theory and practical use. That attitude still helps guide current developments.

The talk reviews why KS-DFT earned its central role and where its shortcomings still matter. Current attempts to improve long-range correlation, reduce cost (e.g., by modern tight-binding approximations), and sharpen robustness will be discussed. I will give special attention to common DFAs (density functional approximations) on "mindless" molecular benchmarks, which probe dark chemical space and expose weaknesses that more curated sets often hide.

Martin Head-Gordon, University of California, Berkeley, USA (Revised February 2026)

From Spectator to Participant: Reflections on My Research in DFT

The rise of density functional theory to prominence in chemistry began in the late 1980s when I was a graduate student working on wave function theory with John Pople at Carnegie-Mellon University. This was before John's limited-term conversion to DFT that is discussed in Peter Gill's contribution. I knew very little of DFT from my training and research as a graduate student. As a fifth-year graduate student, I first heard Axel Becke speak at the 1989 Sanibel Symposium in Florida; it was an exciting talk on fully numerical evaluation of the Kohn–Sham energy.[43] Notwithstanding this encounter, I then went back to my own research and did not engage deeply with DFT until about four years later. This partly reflected my wave function-based training; that type of training, with its strong emphasis on first principles and systematic improvability, kept DFT's rocky path to acceptance in quantum chemistry unpaved for so long (see Jan Baerends's and Bob Jones's talks).

After a few wonderful years learning how to simulate gas–surface interactions as a postdoc with John Tully at Bell Labs, I was fortunate to start my own career in 1992 as an assistant professor in the Chemistry Department at Berkeley. As one research direction, I returned to computational quantum chemistry to work on wave function (specifically coupled cluster) approaches to electronic excited states. This was despite the exciting breakthrough in the accuracy of DFT for ground states reported by Becke[23] at the historic 1991 International Congress of Quantum Chemistry (which I did not attend). Those key early developments did inspire John Pople and countless others to join the implementation, assessment, and further development of DFT. Initially, I watched from the sidelines with interest.

I was first drawn away from the sidelines by a messy software divorce. In my former group, Benny Johnson and Peter Gill decided to break away from Gaussian Inc.'s orbit, as they (and John Pople himself) became disaffected by how they felt developers outside the inner circle were being treated. Naively (at least in retrospect), I thought I could collaborate with both Gaussian and the new venture, Q-Chem Inc. I rapidly discovered this was impossible, and Berkeley (and I) lost access to Gaussian, and thus I became "Gaussian-free in 1993" (i.e., banned by Gaussian, as it was later referred to). In mid-1993, I chose to join the new Q-Chem software venture to embrace the opportunity, as well as the challenge, of building everything from scratch.

Given its mushrooming popularity, DFT was to be at the heart of Q-Chem. Seeking faster DFT, Peter told me about Greengard and Rokhlin's exciting work on the fast multipole method (FMM) for evaluating the gravitational interactions of n-particle systems in linear scaling [i.e., O(n)] compute time.[44] We agreed that a new student in my group, Chris White, would implement the classical FMM for charge–charge interactions, and we would then seek to generalize it to continuous charge distributions. This was an exciting and productive collaboration in which Chris's thesis work was crucial for achieving O(n) evaluation of DFT energies with controlled accuracy.[45,46] In the late 1990s, my then-postdoc Christian Ochsenfeld achieved a conditionally O(n) evaluation of exact exchange,[47] as needed for hybrid functionals. In these efforts, I accepted modern DFT and its successes and limitations as they were (i.e., leaving BLYP and B3LYP exactly as Axel Becke provided them) and concentrated on the question of efficient implementation. By 1996, DFT was fully accepted in chemistry; efficient algorithm development in usable software was one key to its acceptance, and ongoing improvements will be important to its future.

My second focus in DFT was on excited states, starting in 1998. As I mentioned above, I was working on more accurate and much more expensive wave function-based methods and was watching the emergence of time-dependent DFT (TDDFT) (e.g., by Mark Casida and the group of Reinhart Ahlrichs). A bright postdoc in my group, So Hirata, very quickly implemented time-dependent DFT in Q-Chem, including the Tamm–Dancoff approximation,[48] and we were impressed at how accurate TDDFT with GGAs could be for complex molecules and radicals that were otherwise computationally out of reach. While TDDFT remains enormously useful, with Dreuw

and Head-Gordon, we later stumbled on its severe limitations for charge transfer excited states[49] due to self-interaction errors (SIEs) that remain a challenge today (for the state-specific alternative, see Weitao Yang's talk).

My third focus, starting in 2006, was on density functional development, due to the arrival in my group of Jeng-Da Chai, an excellent postdoc who really wanted to work on this problem. We were now in the era of abundant numbers of semi-empirical functionals, often also with abundant numbers of fitted parameters (e.g., ~50), that were determined from limited training data (often without test data). Was it possible to contribute something useful in this context? Jeng-Da and I iterated together toward an approach to functional design that was directly inspired by Becke's "basis functionals," exemplified by the B97 family.[50] Knowing about the SIE issue, I wanted the functionals to use range-separated exact exchange (pioneered by Andreas Savin, Peter Gill, and others) that included 100% exact exchange in the long-range. We also wanted to include dispersion corrections, which were known to be essential for non-covalent interactions, and, if treated via atom–atom C6 potentials, carried no computational cost. There were two useful innovations. First, we optimized all parameters simultaneously; this was the first time this was done with dispersion and range-separation included together. Second, with an eye on the overfitting problem, we did not use all our data for fitting. We held back some data to assess the transferability of the fits, as we expected that using too many fitting parameters would damage transferability. This work produced the wB97X[51] and wB97X-D[52] functionals, two range-separated hybrid (RSH) GGAs that have become widely used. We stood on the shoulders of others in this research: Axel Becke for the semi-local form and exact exchange, Andreas Savin and Peter Gill for range-separation, and Stefan Grimme for empirical dispersion. Yet the result was something new and useful.

I left functional development for a few years until the very talented doctoral student, Narbe Mardirossian, joined my group. Between 2013 and 2018, Narbe and I developed and applied a data-centric strategy that we called "survival of the most transferable" (SoMT) to train Becke-type basis functionals. The main goal was to explore the functional space of basis functional *meta*-GGAs,[53] which has fantastically high dimensionality. We later learned that SoMT was closely related to the forward subset selection algorithm to approximately solve the best subset selection problem. Applied to density functional design, SoMT meant training candidate functionals with different numbers of parameters on about 20% of our 5000 chemical energy differences and then selecting the most promising candidates based on performance on held-back validation and test data. This avoids over-fitting and leads to a functional that aspires to be most transferable from training data to unseen data. In addition to the SoMT protocol, we made three other improvements: (i) we used Vydrov and Van Voorhis's VV10 van der Waals density functional ("−V") instead of empirical damped C6 potentials ("−D"), (ii) we included constraints to obey exact conditions, and (iii) we included restraints to ensure the functionals could be accurately integrated with finite quadrature grids.

The results for predicted molecular energy differences were very good. At the RSH GGA level, SoMT was a direct search over about 100 000 candidates to yield the wB97X-V functional.[54] This functional substantially improved and largely replaced wB97X-D, with fewer parameters, less quadrature error, and better accuracy, particularly for noncovalent interactions. At the RSH mGGA level, there was much more scope for improvement. A screen of some 4 trillion candidates yielded the wB97M-V[55] functional (a representative of the most transferable, at least), which is now widely used. As the first semi-empirical *meta*-GGA designed for transferability, it yielded significant improvements in accuracy over earlier hybrid mGGA alternatives while using roughly three times fewer fitted parameters, being easier to integrate adequately, and obeying five exact conditions. We also used SoMT to design a *meta*-GGA, B97M-V,[56] and a very good double hybrid functional, wB97M(2).[57] The names reflect the intellectual debt I felt I owed to Axel Becke for pioneering the basis functional approach. At the same time, our data science approach broke new ground in functional development with clear benefits.

By the time we developed these functionals, Axel Becke had migrated away from his basis function approach that we had followed. Instead, he pursued (with his usual great insight) post-Hartree–Fock functionals that are closer to non-empirical, as is documented both in his publications and in the talk he presented at the meeting. This reflected Axel's unease about the appropriate extent of semi-empiricism in functional development (see also Peter Gill's comments on John Pople's unease and Gustavo Scuseria's talk). In my research, I have migrated from a DFT spectator trained at the end of the "pure wave function" era of computational quantum chemistry to a participant in modern density functional development. In doing so, I believe that formal rigor (exact conditions) can only help so much with approximate functionals, and so, together with wonderful co-workers (including those working on our next generation ideas), I have tried to directly face the question of how best to realize practical semi-empiricism from a data science and statistical learning perspective.

DFT exploded into chemistry with Axel Becke's invention of hybrid functionals such as B3LYP in 1993 and the ready availability of software such as Gaussian 92/DFT from John Pople's group. Much progress has been made since then, and much of it has stemmed from Axel Becke's ideas. From my own work, for example, wB97M-V has reduced the width of the error distribution associated with B3LYP for chemical energy differences by a factor of about 2.5.[57] Progress will surely continue, and it will be exciting to see what the future of DFT holds. For example, how will progress be made on DFT's remaining challenges of self-interaction error and strong correlations, and how will DFT's synergies with machine learning best be realized? Some of the other abstracts offer specifics on these topics!

Trygve Helgaker, University of Oslo, Norway (Revised January 2026)

Density Functional Theory: Beauty and the Beast

Resistance to new methodologies is common in science. In the 1980s, for example, coupled-cluster theory faced significant opposition from quantum chemists accustomed to linear expansions and the Rayleigh–Ritz variation principle. Similarly, Kohn–Sham DFT was met with deep skepticism by most quantum chemists, but more fiercely and perhaps for more complex reasons. Before the introduction of the generalized gradient approximation (GGA) in the early 1990s, with essential contributions from Axel Becke, DFT's

low accuracy for molecular systems was the main reason. As accuracy improved with the introduction of GGA functionals, critics pointed to its reliance on adjustable parameters and its lack of systematic improvability, in contrast to the zero-parameter wave function-based methods, such as many-body perturbation theory and coupled-cluster theory.

Having been raised on systematic improvability and zero parameters, my initial reaction to the DFT revolution around 1990 was to keep calm and carry on. Still, I was sufficiently intrigued to sit in on Nick Handy's lectures on DFT at the European Summer School in Quantum Chemistry, where I myself lectured on molecular properties. At Nick's invitation, I spent the academic year 1999–2000 in Cambridge, where I incorporated DFT into our molecular electronic-structure code DALTON and performed the first DFT calculations of NMR indirect spin–spin coupling constants.[58] To my surprise, DFT accurately and effortlessly reproduced experimental NMR spectra for systems where the Hartree–Fock method had failed miserably and for which the more complex and more expensive MCSCF approaches were required instead.[59]

The proof is in the pudding: over the next few years, I came to appreciate DFT's usefulness not only for electronic energies but also for molecular properties such as those that describe the magnetic resonance experiments and optical activity. Still, I remained ambivalent to DFT because of the proliferation of approximate exchange–correlation functionals tailored to specific applications. This was for me the beast of DFT.

In 2003, I encountered Lieb's fundamental work on DFT[60] and learned that the universal density functional is nothing but the Legendre–Fenchel transform of the ground-state electronic energy, predicated on two simple properties of the groundstate energy—namely, its continuity and concavity in the external potential. I realized that *DFT is not so much an invention as a discovery*. Whereas the celebrated Hohenberg–Kohn theorem[6] seemed a bit mysterious to me (albeit simple to prove), Lieb's treatment made the theoretical framework of DFT crystal clear and, thus, revealed to me the beauty of DFT.

In my talk, I reviewed some aspects of DFT related to my engagement with it. My first work in DFT followed from the implementation of Kohn–Sham theory in Dalton and involved the extension of DFT to the calculation of various molecular properties.[61] In 2009, we presented the first high-level *ab initio* calculation of the universal density functional and of the adiabatic connection for molecules, including a study of the dissociation of H_2.[62] Later, we introduced Moreau–Yosida regularization of DFT, making the everywhere discontinuous universal functional everywhere differentiable,[63] in this manner also formally solving the v-representability problem of Kohn–Sham DFT. From a more practical point of view, we studied the extension of DFT to magnetic fields,[64] comparing current DFT (CDFT) with magnetic-field DFT (BDFT).[65,66] Comparing various variants of DFT with coupled-cluster theory in a magnetic field by means of the Lieb variation principle, we established the reliability of *meta*-GGA functionals in strong fields,[67] using this level of theory to study molecular properties in ultra-strong magnetic fields.[68]

Erin Johnson, Dalhousie University, Canada (Revised December 2025)

A Canadian Perspective on the Rise of Density Functional Theory in Chemistry with a Focus on Intermolecular Interactions

I was first exposed to DFT in 1999 from the perspective of a user of the methodology, applying it to study the chemistry of organic radicals. As modeling the electronic structure of such molecules with correlated-wave function theory was completely prohibitive at that time, DFT was the natural method of choice. Using hybrid functionals of the type developed by Axel Becke, we were able to compute bond dissociation energies of organic molecules to a level of accuracy rivaling that of correlated-wave function theories in most cases, at a fraction of the computational cost. However, this work revealed some key limitations of the available density functionals: delocalization error led to systematic overstabilization of the pi-conjugated allyl and benzyl radicals, while neglect of London dispersion led to destabilization of molecules with significant steric clashes. I later conducted a systematic assessment of the performance of all density-functional approximations available in the Gaussian03 program for van der Waals complexes and found that none included the necessary long-range attraction arising from London dispersion. This research inspired me to seek to develop improved DFT methods capable of greater chemical accuracy, and I approached Axel Becke about completing a PhD under his supervision. I was particularly motivated to develop a DFT method that was broadly applicable to intermolecular, as well as intramolecular, chemistry. Over the course of my PhD, from 2004 to 2007, Axel Becke and I published a series of papers describing our development of a density-functional model of London dispersion. This model, and other related dispersion corrections (such as those developed by the groups of Stefan Grimme and Alexandre Tkatchenko), are now routinely used in virtually all molecular DFT calculations. As an illustrative application, dispersion-corrected DFT has enabled first-principles prediction of molecular crystal structures to be sufficiently reliable that it has become an applied technology employed in the development of new solid-form pharmaceuticals.

This talk will cover what I consider to be the key advances that led to the rise and widespread adoption of DFT during the late 1990s and early 2000s. These will include triumphs of hybrid functionals for the accurate calculation of bond dissociation enthalpies and other thermochemical properties. I will also highlight some landmark papers that illustrated the neglect of London dispersion within popular functionals and review the development of dispersion corrections, which allowed the extension of DFT from intramolecular to intermolecular chemistry.

Robert O. Jones, Forschungszentrum Jülich, Germany
(Revised November 2025)

50 Years in Density Functional Theory

Our first contact with density functional theory grew out of a surface physics project with John Harris. Calculations of the surface energies of model metals had led to widely differing interpretations, and John Harris and I were convinced that "inhomogeneous electron gas" approximations used in calculations by Lang and Kohn (1970) could not possibly work for regions so far away from their regions of obvious validity. The astonishing results of our calculations of exchange and correlation energies for a jellium half-space

model demanded that we seek the reasons why a local density approximation could give useful answers. The unexpected result that the local density approximation often gave reasonable results for small molecules was a prerequisite for the ultimate success of DFT in chemistry. The lasting contribution of that paper was the first use of "adiabatic connection" in DFT.

The focus of my presentation is, however, on the 15 years that followed and the negative reaction of most theoretical chemists toward the few practitioners of density functional or Hartree–Fock–Slater calculations for molecular systems. Contributing to this reaction were certainly the overselling of Xα methods, the lack of familiarity of chemists with the electron gas models and the numerical methods used by the condensed matter physicists, queries about mathematical rigor, etc. I remain perplexed, however, over the hostility shown by so many over such a long period toward a method that now dominates practical computational chemistry. I shall outline my own experiences and look forward to hearing the insights of others.

Of course, the development by Axel Becke in the late 1980s of non-local approximations for exchange was absolutely essential to the breakthrough of DFT in chemistry after 1990.

John Perdew, Tulane University, USA (Revised November 2025)

Almost Present at the Creation: How the DFT Ladder was Built

The fundamental work of Kohn and Sham was published in 1965, the year I started graduate studies in physics, but I did not know about it for seven more years. I will discuss why density functional theory had a slow start in solid state physics and the work of Lang and Kohn in 1970–1971 that finally caught the interest of many physicists. I will also discuss Jacob's ladder of density functional approximations, all building on the local spin-density approximation of Kohn and Sham, which eventually captured the interest of chemists as well. I will stress the key, but largely unsung, role of David Langreth, who discovered early exact constraints and designed an early generalized gradient approximation, the work of Olle Gunnarsson and Bengt Lundqvist, and the work of theoretical chemist Mel Levy, who generalized and simplified the early proofs of the Kohn–Sham theorem and discovered many more exact constraints. I will further pass on historically relevant anecdotes from or about Walter Kohn, Lu Sham, Axel Becke, Gabor Csonka, John Pople, Nick Handy, Bing Copilot, and others. As time allows, I will mention current work on self-interaction correction and the non-empirical semi-local approximations LSDA, PBE, and r^{2}SCAN.

I was saddened by the passing of Axel Becke, a creative giant in our field of density functional theory. Axel did early work on the generalized gradient approximation (GGA) and pioneering work in the development and testing of higher-level approximations to the exchange–correlation energy, including *meta*-GGAs, global hybrids with partial exact exchange, and long-range van der Waals corrections. Many of his papers were single-authored works in which he did everything from the spark of the idea to the coding, testing, and writing. So far as I can tell, he was the most influential of several theoretical chemists who persuaded John Pople to try density functional theory, leading to a sea-change and a Nobel Prize in chemistry. It was always worthwhile and enjoyable for me to talk with him at meetings. While his focus was on making density functionals more accurate, he had great insight into the underlying theory. At the end of his career, as at the beginning, he preferred density functionals with few parameters that could be estimated by insight and fine-tuned by fitting to molecular data.

Dennis Salahub, University of Calgary, Canada (Revised January 2026)

From Muffin Tins to Robots—7 Decades of DFT

Arguably DFT (Kohn–Sham) had its origin in Slater's 1951 paper on local electron gas exchange as an approximation to Hartree–Fock theory (I do not think Slater would have called it DFT…), which provided the basis for the Xα method, which was introduced into chemistry with the Xα Scattered Wave method that used a so-called muffin-tin potential, providing spherically symmetric solutions on radial grids. My talk traced some of the history of DFT through the 1960s and 1970s, showing how the $X\alpha - SW$ method opened doors and attracted chemists, particularly for transition metal systems. It still strikes me that there was an enormous amount of good science done with DFT in the thirteen year period between Slater's seminal paper and the Hohenberg–Kohn and Kohn–Sham papers. In addition, like John Perdew, I was blissfully unaware that I was doing DFT calculations for many years before I became aware of the HK and KS papers. One can only wonder how the field of computational "DFT" in chemistry and physics would have evolved if the HK and KS papers had never appeared. Moving into the 1980s, techniques from quantum chemistry, notably Gaussian basis sets, took the forefront along with ever-improving exchange–correlation functionals. Axel Becke's work personified the "ever-improving" aspect of this statement. From GGAs to hybrids to, most recently, local double hybrids, Becke's work led us relentlessly to better functionals based on good physics with a minimum number of parameters, for the most part. In my view, and without denigrating the work of many others who have contributed substantially, Becke and John Perdew have been the master builders of new, improved density functionals over the last four decades or so.

I then fast-forwarded to today with the advent of artificial intelligence, machine-learning, and quantum computing. Example applications were drawn from our own work, with apologies to the myriads of others whose work is even more exemplary. In a nutshell, I tried to show the power of DFT-centric methods for an eclectic variety of chemical processes in complex environments (Born–Oppenheimer MD, multiscale QM/MM, RTTDFT for attoscience, machine-learning accelerated discovery of new materials, quantum machine-learning, etc.). All of these depend, in the final analysis, on having density functionals of sufficient accuracy along with implementations of sufficient speed and using the eminent interpretability of an orbital-based mean-field theory (KS-DFT).

So how might this play out in the future? I think that two overarching developments will determine how DFT evolves and, indeed, whether it survives as a primary computational tool for chemistry, physics, materials science, and biology. First, the advent of the age of artificial intelligence and machine learning is already having a profound effect; see, just for one example, the recent Microsoft ML-derived functional that beats all records for organic chemistry (but at

what price for interpretability?). Second, and still more embryonic, I think, significant progress toward practical quantum computers has to be taken into account, in my view. If (when?) the day comes that a quantum computer can efficiently provide high-accuracy energies and wave functions for complex systems, including those with strong correlation, will there be any need at all for DFT? The answer may well be "no" as far as energies, densities, and other properties (all calculable from the wave function) are concerned, but I still see a need for something like DFT for interpretability. Perhaps many, or all, of the conceptual DFT tools used today, including Axel Becke's ELF (Electron Localization Function), will survive in the post-DFT world. One thing that does seem clear to me is that the level of excitement and creative perplexity raised at this symposium bodes well for the future of DFT-centric science, whatever form that may take.

Andreas Savin, Laboratoire de Chimie Théorique, CNRS and Sorbonne University, Paris, France (Revised January 2026)

DFT: Pro and Con Arguments

The first part of the talk discusses the scientific opposition to density functional theory. It is mainly based on points raised in Ref. 75.

The second part of the talk discusses human and social aspects of acceptance or rejection following the paper Ref. 76.

What follows here is a revisit of my talk in the light of the 15 months that have passed. Axel Becke participated in the Stockholm symposium. One year later, we had the sad news that he had passed away. In hindsight, I decide to concentrate on the central question of this symposium ("Why did it take so long for DFT to be accepted in chemistry?") and stress Axel's paramount importance in making it accepted.

Density functional theory (DFT) has been present in chemistry and has shown some good results since the 1970s. This can be seen, e.g., in the review in Ref. 77, Sec. IV B. Parr was also a highly respected quantum chemist. His well-known book on DFT, written with W. Yang, also came out in 1989. In spite of documented successes, there was a delay in having density functional approximations (DFAs) widely accepted as a tool in chemistry. Why?

Is DFT not well founded? I do not think that anybody has doubts about the Hohenberg–Kohn theorem, but R. Ahlrichs once told me that this theorem and DFAs are different things. This viewpoint was once one of the points of criticism made in Ref. 75. However, I see this as a general problem in quantum chemistry: we do not have useful bounds for the results our calculations provide. I still believe that there are several aspects of DFT that need to be developed. I presented some in my talk, but I will stay now with the historical perspective that was the main topic of the symposium.

In the absence of bounds, how do we know that our results are good? Or, as Walter Kohn once put it in a private conversation, "Without experiment they would not know if their results are right or wrong." Important people in the DFT community did not see the need to be convinced. For example, in 1989, Salahub told me that he was more interested in using DFT for interesting applications or further improving it (he later introduced corrections for dispersion interactions). The same year, Ziegler started his presentation at the 10th Canadian Symposium for Theoretical Chemistry (Banff) by saying.

The question is not "Do the density functionals work?" We know they do. The question is, "Why do they work?"

However, there is a different attitude, currently widely accepted through machine learning: to demonstrate the validity of approximations through statistics. J. Andzelm and E. Wimmer did it using the DGauss program and the power of Cray computers. This is also how Axel Becke convinced John Pople about the usefulness of DFAs by using John Pople's own dataset, G-1.[23]

Is the acceptance of the DFAs due to the introduction of the generalized gradient approximations (GGAs)? A change in perspective about what DFAs are started in the mid-1970s, namely, that they model the exchange and correlation hole. Axel also contributed to this viewpoint, e.g., in Ref. 78. During the 1990s, a new convert to DFT told me that the GGAs convinced the chemistry community about the usefulness of DFT and that it is natural that it takes some time for ideas to penetrate the scientific community. It might be true, but I do not think it is the only reason.

I think that there is a human and social factor that plays a role. In my presentation, I followed some points I found in the paper by Bang and Frith cited above. I now stress only one of them; decision inertia (that people tend to repeat past choices regardless of current evidence) seems an explanation for the difficulty of accepting DFAs. The persistence within quantum chemistry of wave function methods is due to the smaller number of electrons of the atoms and molecules dealt with at the time. These methods were not applicable to the systems of solid-state physics, in which field DFT had much earlier become "the method of choice." As quantum chemists became interested in ever larger systems, they were hampered by the rapid growth of the computational demands of their traditional methods, and they became interested in the more efficient DFT. It produced a revolution. A colleague of mine told me around 1993: "DFT has changed my life. I can now treat systems I could not treat before."

Interestingly, DFT was recognized by a Nobel Prize in chemistry (and not in physics), and Axel Becke played a decisive role in changing the direction of chemistry. A truly successful scientist must be able to see the field of research from a new perspective, recognize the important challenges, be open to new ideas, and have the persistence to achieve great goals with them. The key to these different aspects of success will vary with the scientist and the epoch. Axel Becke can be seen as the epitome of the successful scientist: Steadfast in his pursuit of better density functionals, accepting the challenges of DFT and enriching this field with new ideas.

Gustavo E. Scuseria, Rice University, USA (Revised January 2026)

The Elephant in the Room: Can DFT Model Entanglement?

I became an enthusiast of DFT early in 1992 when John Pople visited Rice and told me about Axel Becke's results presented at ICOC 1991 and his own BLYP benchmarks. At the time, I was involved in coupled-cluster theory and had already implemented CCSD(T) energy and gradients for large basis sets, including an open-shell formulation. A barrage of results obtained with these

codes showed that such a model could achieve chemical accuracy for molecules in the upper part of the periodic table. This feat would later become known as the "gold standard of quantum chemistry," a term I did not coin and do not share without adding the qualifier "for weak correlation." Soon after Pople's visit, I implemented BLYP and published a paper comparing it (with HF orbitals) with CCSD(T). I showed that they were roughly the same quality for many important problems, including activation barriers. A few years earlier, C_{60} had been discovered at Rice, and I was interested in carbon nanostructures; coupled-cluster was not an option back then, and this is how my DFT adventure began.

I met Andreas Savin and John Perdew a few years later, and they became great collaborators. Many functionals that bear my name were developed with them or, in some cases, such as HSE, influenced by Savin's ideas on range separation and Axel Becke's foundational concept of introducing a portion of Hartree–Fock exchange in DFT. A couple of decades later, I became disenchanted with DFT when I realized that the great challenge that strong correlation poses to electronic structure theory was not easily addressed with DFT. Even worse, the way forward in DFT was by adding pieces of wave function theory, but the latter lacked a solution for strong correlation, a regime where entanglement and degeneracy are ubiquitous, and single-determinant symmetry-adapted coupled-cluster theory fails miserably.

The weak correlation problem, the perturbation regime where broken-symmetry mean-field theory is qualitatively correct, has been solved by the universal coupled-cluster prescription. Strong correlation is a different story, with a happy ending still unclear. Strong correlation is a non-perturbative regime where broken-symmetry mean-field theory is incorrect and does not fully reveal the effects of entanglement or near-degeneracy. It is much broader than the molecular dissociations that UHF or GHF can qualitatively describe. Strong correlations intertwine with weak correlations (e.g., superexchange) and are pervasive in many chemistry and condensed matter physics areas.

This talk will discuss why I embraced and later defected from DFT. I will also briefly describe my ideas for a universal solution to strong correlations based on dualities that modify or eliminate entanglement. This framework may enable novel routes for DFT and free it from what, in my opinion, is its current stagnant situation.

David J. Tozer, Durham University, UK (Revised June 2026)

DFT: Recollections and Wave Functions

In 1991, I was a Ph.D. student with Nick Handy in Cambridge, working on correlated wave function methods. John Pople visited in December of that year and suggested that Nick should investigate DFT because Axel Becke's results were so promising. My Ph.D. project then took a rapid change of direction!

In my talk, I provided some personal recollections from this period, when so many chemists started paying attention to DFT. I also briefly described our fledgling attempt in 1996 to use a neural network to construct an exchange–correlation functional,[69] a study that has acquired newfound relevance in the AI boom. That neural network local functional was trained on accurate exchange–correlation potentials from correlated wave function densities. Despite the simplicity of the neural network, geometries were comparable to those from the local density approximation, and orbital energies were much improved for systems adequately represented in the training set. We also considered the possible extension to the generalized gradient approximation. A more extensive investigation was provided in Ref. 70.

Training that neural network relied upon knowledge of correlated wave functions. Looking to the future, I presented another example where correlated wave functions provide key insight and new numerical data, which may aid the development of DFT functionals. In particular, I described our recent work considering classical reaction barriers in DFT from the perspective of the density-fixed adiabatic connection.[71] I showed how our newly introduced reaction adiabatic-connection integrand provides a simple way to visualize and understand functional-driven errors in barriers from approximate functionals, clearly separating the roles of exchange and correlation.

Weitao Yang, Duke University, USA (Revised May 2026)

DFT: Advances in Functional Approximations and in Theory of Excited States

The foundations of density functional theory (DFT) for describing ground states were established by Hohenberg, Kohn, and Sham in 1964–1965. The accuracy of DFT predictions hinges on the quality of density functional approximations (DFAs). While the local density approximation (LDA) was developed in 1965 and the Xα model in the 1950s, DFT faced significant resistance from many chemists until the late 1980s and early 1990s. Practical minds found the accuracy unconvincing, while theoretical minds were hindered by the functionals' lack of N-representability, a longstanding issue rooted in the challenges of reduced density matrix theory from the 1950s. I will recount a personal encounter with such resistance.

Advances in generalized gradient approximations (GGAs), particularly BLYP and PW in the late 1980s, coupled with developments in numerical methods and computational implementations during the same period, ignited a surge of interest among chemists and overcame the resistance. I will elaborate on the development of LYP. Subsequent advancements in GGAs, hybrid functional approximations, range-separated functionals, and the inclusion of van der Waals interactions have brought DFT to its current prominence as a cornerstone of computational chemistry and materials science.

Despite advancements, significant systematic errors persist, such as underestimating energy gaps in molecules and materials, incorrectly predicting the dissociation limits of chemical bonds, over-delocalizing charge distributions, and misaligning energy levels at interfaces. These errors stem from the violation of exact conditions on fractional charges and spins, which are consequences of quantum mechanical degeneracy manifested in the classical variable of electron density. Our recent advancements addressing the delocalization error have elevated DFT to a new level of robustness and accuracy, broadening its applicability. Particularly, overcoming the delocalization error leads to orbital energies accurately approximating ionization energies and electron affinities to ground and excited state removal and addition states. Furthermore, since the

1970s, Kohn–Sham functionals have been employed for ΔSCF calculations of excited states, achieving accuracy comparable to ground state results, despite a lack of theoretical justification. These observations indicate that the functionals theoretically formulated and approximations constructed for ground states contain excited state information.

Indeed so. We establish the theoretical foundation for ΔSCF calculations of excited states, showing that it is necessary to go beyond electron density and use the first order density matrix of the noninteracting reference system to define the energy functional. While the minimum of this functional corresponds to the ground state energy, consistent with ground state DFT, the stationary solutions yield excited state energies and electron densities, consistent with ΔSCF calculations.

I was deeply saddened by the passing of Axel Becke, a towering figure in density functional theory. I had the privilege of first meeting him in 1985 in Kingston, an encounter that left a lasting impression on my scientific thinking. Even at that time, he was already developing the ideas that would later crystallize into the generalized gradient approximation. He later made many breakthroughs in developing DFT. His conceptual clarity and enduring contributions continue to shape the field and inspire generations of chemists.

Additional Contributions

Sture Nordholm, The University of Gothenburg, Sweden

Summary of the DFT Symposium and Reflections on the Full Circle of Axel Becke

The contributions to this symposium illustrate the close connection between physics and chemistry in the field of electronic structure of atoms, molecules, and materials: The same general area of application is theoretically developed in both disciplines but with differing emphasis. In the perspective of physics, electron gases and dense electron fluids neutralized by cations in solid materials, i.e., many-electron systems, play an important role in the development of theory, while chemists are interested in atoms and molecules, initially involving relatively few electrons, as well as the various types of chemical bonding between the atoms by which the molecules form. It is not surprising that these differences in perspective caused physicists to turn to density functional theory earlier than chemists, who went from small atoms H, He, Li, etc., to corresponding molecular structures H_2^+, H_2, He_2, Li_2, etc., in the early years of quantum mechanics. They discovered the mathematical and numerical beauty of Hartree–Fock theory, which became the foundation of "quantum chemistry," but knew from the beginning that it had a "dissociation error" in the description of most covalently bonded molecules: it did not apply, in its simplest form, to the free atom limit, which effectively constituted a "correlated system." The valence bond (VB) theory of Heitler and London in 1927[72] offered an early solution, which preoccupied many chemists due to its simple physical logic, but computational convenience drove most quantum chemists in the direction of Hartree–Fock (HF) theory, followed by configuration interaction (CI), in order to efficiently address the need for electron correlation. This became the "*ab initio* pathway" to quantum chemistry, and, together with the finite basis set method and the variational principle, it offered a reliable computational approach to increasingly accurate molecular properties.

The only problem was that this *ab initio* approach was computationally demanding, with correlated calculations increasing the computational cost by orders of N^4, N^5, or higher (exponentially for the full solution), where N is the number of electrons. However, the computers got better year by year, and the quantum chemists shared their computational advances among themselves so that larger systems could be studied and higher accuracy achieved at a quite reasonable pace. Why should this safe "*ab initio* pathway" be abandoned for the many unknowns of DFT? See the talks of Jones, Helgaker, and Savin for a discussion of the barrier between physicists and quantum chemists in the early years of DFT.

The "year of DFT" arguably fell between the proof by Hohenberg and Kohn in 1964[6] that it is possible to determine the ground state structure and energy of an electronic system formed by atoms by minimizing an energy functional in terms of electron density only and the recommendation by Kohn and Sham a year later[7] that it be done in terms of a density described by orthogonal one-electron orbitals. (See Becke, Burke, and Perdew.) This allowed the kinetic energy to be determined in the manner of the quantum mechanics of corresponding independent electrons, and it was, in fact, the start of the "full DFT circle of Axel Becke." However, this circle was unheralded at the start. Not all physicists and almost no chemists had taken notice of the original Thomas–Fermi DFT, without reference to any wave functions, which had been proven unable to predict covalent bonding and thereby disqualified itself from most chemistry. After many years of Thomas–Fermi theory, the HK theorem suddenly showed that, while TF-DFT may be in error for the most fundamental part of chemistry, it was now known to be possible in principle to correct this error and find a Hohenberg–Kohn form of density functional theory (HK-DFT) that gave the right answer for the ground state energy in terms of electron density only. This would seem a great change of fortune for DFT, but, oddly enough, it took only a year for Kohn and Sham to suggest that HK-DFT was not a realistic option. In retrospect, the wave function theory was needed to allow the kinetic energy to be obtained by quantum mechanics. The Kohn–Sham DFT (KS-DFT) launched this way was, in fact, quite like the Hartree–Fock–Slater method (Slater[8]) in which the Hartree–Fock exact exchange was treated by local approximation. The KS-DFT has become the foundation of modern electronic DFT, despite its fundamental dependence on orbital wave functions, in contradiction to the "density only" DFT proved possible in the work of Hohenberg and Kohn. This fact has not been noted and discussed enough (see, however, the talk of Salahub), it seems, but it was the start of the circular motion of DFT from a density only form to a hybrid "wave function/density" (W/DFT) form where, initially at the behest of Kohn and Sham, the kinetic energy retained its wave function evaluation from original Schrödinger quantum mechanics.

For several reasons, the dramatic advance of HK-DFT, being possible in principle (1964) but then rejected in KS-DFT (1965), did not bring about the expected theoretical debate. Possibly this was because physicists in the field had already explored Hartree–Fock–Slater (HFS) models, which looked much the same as KS-DFT, and most chemists were still doing *ab initio* wave function theory and did not pay much attention. The theoretical foundations had changed greatly, but the practical work was not much affected. Physicists (see the talks by Jones and Perdew) continued

developing what could now be referred to as KS-DFT by use of local density approximation (LDA), refining it to account for the presence of two spin fluids (LSDA). In the 1970s, the HFS method had been refined into a parameterized Xα theory, which was widely promoted and used. (See the contribution by Schaefer below.) The applications of these methods to problems of chemical interest were sometimes beset by errors related to the numerical procedures, which were not fine-tuned for the chemical system. Stories of "DFT" producing linear water molecules and related oddities in some of the reported calculations (but far from all; see the talks of Baerends and Jones) made the rounds among quantum chemists, making them less inclined to leave their *ab initio* pathway. For a discussion of the conformity of collective decisions, also in communities of natural scientists, consult the talk of A. Savin.

Axel Becke (see also the talks of Baerends, Burke, Jones, Perdew, and Salahub) came into the field of electronic DFT for chemical applications from theoretical physics and brought with him experience with Hartree–Fock–Slater model calculations and parameterized Xα models. His first major contribution was to devise new numerical methods to eliminate the numerical errors that had beset test calculations for chemical systems. Thus, he reliably concluded that simple LDA implementations of KS-DFT did improve results obtained from Hartree–Fock theory for covalent bonding (by nearly an order of magnitude) but not enough (another order of magnitude to reach "chemical accuracy") to raise serious interest among chemists. The underlying fundamental point here is that Hartree–Fock theory, for all its merits, has a weakness in that atoms (apart from inert gas and alkaline earth atoms) are not consistently treated independently and collectively in molecular dissociation. This "dissociation error" of HF theory is "non-local" in the calculation for a molecule and, therefore, in principle, absent in the local approximation of exchange–correlation in LDA forms of KS-DFT.

The error of Hartree–Fock theory for greatly expanded molecules arises because the bonding electrons do not move independently among the atomic sites as the theory assumes. This fact focused the attention of chemists on "electron correlation" (the pairwise or higher order interdependence of electron motion) and established the HF + CI level of theory as the standard for chemical applications. The more approximate LDA form of exchange fortuitously avoided the dissociation error of HF theory but introduced other large errors. To raise interest among chemists, the total error had to be decreased by at least an order of magnitude for KS-DFT to become competitive with the HF + small CI standard of quantum chemists. The next idea of Becke and others at about the same time (see the talk by Perdew for the parallel development of a Jacob's ladder of theories based on the satisfaction of physical constraints) was to let the previously local exchange become non-local and include electron correlation of Coulombic origin.

A simple way to include nonlocality in an energy functional is to let the local expression in electron density become the first term in a Taylor expansion continued to the second term. The next term involves the gradient of the electron density. One expects a large gradient (i.e., rapidly changing electron density) to imply a large correction, while a small gradient (nearly constant electron density) implies that the local approximation is more nearly valid, with corrections due to nonlocality likely to be small. Thus, it would seem likely that one may find a parameter by which to multiply the linear gradient correction to significantly improve the accuracy over LDA. Becke constructed several successful gradient corrected energy density functionals in the mid-1980s and late 1980s. The term "generalized gradient approximation" (GGA) was coined (by John Perdew, it appears) for the many non-local approximations of this type that appeared.

The GGA corrections proved quite successful, and the breakthrough was now near. Another possibility for "a year of DFT" is 1988, when Axel Becke published both his new numerical integration method for DFT and his successful functional B88 based on the use of GGA. A few years later, Becke managed to show leading theoretical chemists (Pople, Nicholas Handy, and others) at a quantum chemistry conference in Menton in 1991 that his results, by KS-DFT(B88) with the inclusion of local correlation, for atomization energies of a large set of molecules were nearly as good as those of much more costly correlated quantum chemical methods. The principle (*ab initio* pathway) was now, in the minds of many quantum chemists, subverted by pragmatism. Such strong evidence of success could not be ignored. Pople (see the talk of Peter Gill) and Handy (see the talk of David Tozer) both had "an abrupt change of heart" and helped usher DFT into the community of quantum chemists. New implementations of DFT soon appeared with numerical refinements suited to chemical applications. In the case of Pople, the conversion to DFT was only temporary according to his collaborator at the time, Peter Gill (see the abstract above and talk), and his preference soon (about 5 years later) returned to the *ab initio* pathway. His Nobel Prize (shared with Walter Kohn as the originator of modern DFT; Pople was cited for his contributions to quantum chemistry) lecture in 1998 dealt nearly exclusively with *ab initio* methodology.

The great success of Becke's B88 functional with local correlation was a surprise to the quantum chemists, and the physical reasons for the remarkable accuracy remain incompletely understood even today (see the talks of Baerends and Savin). The treatment of the nonlocality of the exchange–correlation hole by GGA became the ladder by which "the genie escaped from the bottle." The quantum chemists got over the barrier from *ab initio* methods to KS-DFT, and this released a torrent of creative modifications (improved numerical methods and functionals) of DFT to suit the many chemical applications waiting for it. A crucial question soon appeared and remains very significant today: How far is it reasonable to allow parameterization and data fitting to go in producing new energy functionals for general or more specific chemical purposes? There may be no simple or definitive answer to this question, but it should be clear that there is great scope for parameterization of the nonlocality of the exchange–correlation energy. The need for parameterization and data fitting in DFT caused serious concerns and disagreements among the quantum chemists (see the talks by Becke, Gill, and Head-Gordon). Axel Becke accepted parameterization, if only in a restrained form, and he much preferred less over more. Physicists naturally preferred physically derived improvements and the application of exact constraints, as in the Jacob's ladder of DFT theories of Perdew and co-workers (see the talk by Perdew). The area of applications for DFT was in the physics community more often centered on the solid state and materials science than on molecules. This led to a greater need for computational efficiency and, in turn, to an acceptance of less numerical precision in the hope that the DFT method would still be mechanistically accurate (see the talk by Jones).

In the early 1990s, Becke took the next major step in his circular route from wave functions to electron density functionals back to wave functions again. See also the talk by Gill. He proposed to use the exact wave function expression for exchange as a partial contribution to the non-local exchange–correlation functional. This can be understood as a step from "near-locality" of the GGAs to a greater range of nonlocality of sound physical origin. Of course, the full Hartree–Fock exchange contains the dissociation error, so one does not expect to use so much of it in an optimized form of DFT, but a minor amount (of a quarter or a third) may still provide significant benefits. The corresponding hybrid form of KS-DFT appeared in 1993. Three related hybrid functionals (B3LYP, B3PW91, and B3P86) were included in the Gaussian94 program, enabling their widespread use by quantum chemists. They significantly improved results in comparison with the earlier nearly local KS-DFT (GGA) at the computational cost of having to do essentially a full Hartree–Fock calculation.

Another significant step in the direction along the circle from "density only DFT" back toward wave function theory had been taken. The term "hybrid DFT" has now come into widespread use, implying the presence of wave function methodology within density functional theory. Somehow this terminology had not previously been introduced, despite the use of orbital wave functions in KS-DFT since 1965. The use of orbital wave functions for evaluation of kinetic energy by the exact quantum mechanical operator had, for peculiar historical reasons, been excluded from the category of "hybrid DFT." There was resistance from the DFT community to the use of exact Hartree–Fock exchange. This practice seemed, to some experts, better seen as a return to Hartree–Fock theory rather than as a new form of DFT.

It should be noted in this context that about a decade before, Stoll *et al.*[73] had developed a form of DFT, which might be called Hartree–Fock DFT (HF-DFT), which was further along the circle back toward wave functions (see the talk by Savin). They proposed to accept HF theory in full but add just electron correlation by density functional approximation. They argued that correlations within spin fluids were insignificant due to the dominant role of exchange–correlation. Thus, they only accounted for the correlation between electrons of opposite spin by a local functional. In many cases, this form of HF-DFT worked very well, but unfortunately, for covalently bonded molecules, it produced shifts in bond length in the wrong direction (shorter than for HF theory rather than longer as needed). The local "between-spin electron correlation" could not correct the dissociation error of HF theory, which is of non-local character. A non-local correlation correction was needed, which was closely coupled to the nonlocality of the Hartree–Fock exchange. A decade later, Axel Becke found a practical solution to this problem, i.e., a small amount of exact exchange combined with gradient corrections for the full exchange–correlation functional. This scheme of error correction for Hartree–Fock theory provided a new and higher standard of DFT accuracy, which took it well beyond that of Hartree–Fock theory itself for atoms and molecules.

Another challenge facing DFT was the inclusion of long-range electron correlation effects needed to account for what chemists generally call "dispersion attractions" between molecules. Physicists typically refer to "van der Waals interactions" and see them as an intermolecular bonding mechanism of physical origin in distinction to the chemical bonding acting within a molecule. Later, in the adaptation of DFT for chemistry, Becke and others (see the talks by Grimme and Johnson) addressed this problem and found multipole expansion methods that worked well. Interestingly, physicists, including David Langreth in collaboration with the group of Bengt Lundqvist in Sweden, developed their own "van der Waals functionals" for the same purpose at about the same time with similar success (see the talk by Perdew). DFT was clearly able to account also for long range correlation effects important in intermolecular interactions and, for large molecules, also in intramolecular interactions.

The success of DFT for chemical applications was now, after the arrival of the hybrid functionals mixing in exact exchange, ensured. Quantum chemists started, nearly universally, to use the KS-DFT option made available in their dedicated program packages such as Gaussian and Q-Chem (Pople, Gill, Head-Gordon, and others) and later Dalton (Helgaker and others). After this arrival in chemistry, the development of DFT has continued (see the talks of Head-Gordon, Scuseria, Tozer, Yang, and Perdew). Much of the effort has gone to the improvement of numerical efficiency, which most immediately determines the range of applicability of DFT in chemistry. The availability of many different functionals with different strengths and weaknesses has also allowed weighted combinations of them to be optimized in comparison with trusted data. New energy functionals may exploit not only conventional parameter optimization but also AI and machine learning (see the talks of Burke, Gori-Giorgi, and Salahub). The physicists in the DFT community have found additional physical constraints to impose on the parameter fitting (see the talk of Perdew). New developments generally take DFT in the circular direction back toward the wave function origin of quantum mechanics by use of additional wave function parts in the "hybrid KS-DFT" form of the theory. Axel Becke spent much time in later years developing functionals, adding density approximated correlation to exact exchange (as in B05 and B13), and ended his talk in Stockholm considering the inclusion of certain forms of correlation also in wave function form. He came ever closer to a complete return to the *ab initio* theoretical base, but only after a magnificent circular journey from wave function quantum mechanics into density functional approximations and, by hybridization of DFT, back to wave functions again.

It seems clear now that all truly successful forms of DFT for chemical systems composed of atoms and molecules share the "common denominator" of some form of hybridization, i.e., input of wave functions. Still further wave function effects have been targeted but largely remain to be incorporated, e.g., excited states, entanglement, and strong correlation (see the talks of Head-Gordon, Yang, and Scuseria). The question of how far to go with parameter fitting has been placed on center stage by the arrival of artificial intelligence and machine learning (see the talks by Burke and Salahub). The advent of quantum computers, particularly suitable for quantum calculations, may further advance the hybridization of DFT. In fact, they may, with their facility for numerical solution of quantum problems, signal a general return to *ab initio* methods (see the talk by Salahub).

The "Hohenberg–Kohn point" on the circle of theory is not, at present, computationally successful, but it is theoretically important, nonetheless. The knowledge that density-only HK-DFT is possible in principle tells us that future progress can be sought not only in the direction of further hybridization to approach the

full wave function theory more closely but also by developing a fundamental new theory with less hybridization to approach the Hohenberg–Kohn "density only" form of DFT (see the talk of Helgaker). Quite likely, the latter will be challenging and, perhaps, mainly produce understanding of quantum mechanics rather than computational advantages. However, we need both computational efficiency and understanding to produce the greatest benefits for all users of electronic structure theory.

Conclusion

The history of density functional theory (DFT) is interesting and subtle. The DFT option was present in the form of Thomas–Fermi theory from the birth of quantum mechanics in the 1920s, but this option was essentially dormant for 40 years, and the TF-theory was more of an interesting oddity than a commonly used tool. It was found unable to account for covalent bonding by Teller in 1962.[5] What set DFT in motion seems (see the talks by Baerends, Jones, and Salahub and a contribution by Schaefer below) to be the famous paper by John Slater in 1951, which showed that the mathematically elegant but numerically demanding (at the time) Hartree–Fock theory was susceptible to physical approximation in terms of simple estimation of the exchange as a function of the local density. This realization produced Hartree–Fock simplifications (HKS, Xα, etc.), which could in retrospect be called early forms of modern DFT but were not so designated. It was only after the Hohenberg–Kohn and Kohn–Sham papers in 1964–1965 that the term "DFT" became established for work of this type. An "inner circle of theory" was established by the work of Slater, Kohn–Sham, and Becke, who started from Hartree–Fock theory, introduced density functional exchange first in local and then gradient corrected non-local form, and then realized that part of the exact exchange was needed for best accuracy. So, the development could be said to be HF → DFT → HF. It is possible to think of modern DFT as an approximate form of Hartree–Fock theory (with correlation nearly always added), and many do, but the common practice is to start from the Hohenberg–Kohn paper and then consider KS-DFT, in its many forms, as an approximation to the true HK-DFT that has not yet been found.

It is, of course, well known that this inner circle of theory must be expanded to include correlation to satisfy the demands of chemical applications. Fortunately, correlation, as defined by quantum chemists (deviation from restricted Hartree–Fock theory), is, unlike exchange, a physical effect (response to electron–electron repulsion) that is, by its foreseeable mechanism, likely to be possible to reasonably estimate by density functional theory and incorporate into a KS-DFT theory. In fact, there is good reason to believe that the total of "exchange and correlation energy" is simpler to estimate than the two energies individually since the physical correlation may be expected to "tidy up" extremes of the statistical/mathematical exchange effect (e.g., localize particularly dispersed exchange holes). It follows that the more relevant "outer circle of theory" includes correlation and takes us from wave function quantum mechanics to density functional theory and back again, WFT → DFT → WFT. Indeed, simple approximations for correlation energy have been successfully included since the early years of DFT.

The "full circle of Axel Becke," i.e., of hybrid wave function and density forms of quantum mechanics suitable for work on electronic structures of atoms, molecules, and substances formed from them, is now well in sight, but much remains to be done to populate it with optimal forms of theory at different levels of hybridization. The "Jacob's ladder of DFT" of John Perdew and his colleagues in the physics community of DFT experts differs mainly in its physical reasoning for the functionals but is otherwise smoothly integrable into this linear space of implementations of quantum mechanics stretching from "wave functions only" to "density only." The different training and domains of application have occasionally caused disagreement, and sometimes even estrangement, between physicists and chemists in this field of electronic structure theory (see the talks of Jones and Savin). In the end, the great progress made and the amicable discussions at this symposium clearly show that the differences have been overcome most successfully. They may even have been productive for the development of DFT in all its forms. Axel Becke, a physicist by origin (see the contribution by Boyd), certainly found areas of communal interest with chemists and constructed a bridge between the perspectives of physicists and chemists. He overcame the reluctance of quantum chemists to broaden their interest from their home ground of *ab initio* wave function theory to include density functional theory. His exemplary research, both stringently logical and original, was found compelling by leading quantum chemists. It will remain an inspiration for us all.

Brief Chronological History of Electronic DFT—From a Chemist's Perspective

1927: Thomas and Fermi show that much of quantum mechanics can be done with electron density instead of wave functions. Proposed TF-DFT is a true (density only) DFT.

1951: Slater shows that mathematically demanding exact Hartree–Fock exchange can be reasonably approximated in terms of simpler local density approximations. Such Hartree–Fock–Slater methods become precursors of modern DFT.

1962: Teller shows that TF-DFT is unable to account for covalent bonding.

1964: Hohenberg and Kohn prove that true DFT, in terms of electron density, is possible for electronic ground states but offer no clue what the functional looks like.

1965: Kohn and Sham suggest that orbital wave functions be used to allow kinetic energy to be determined quantum mechanically in DFT. KS-DFT is born.

1970–1990: Quantum chemists generally (not all) resist DFT in all forms (TF, KS, HKS, and Xα) because they are not "*ab initio*" and not accurate enough.

1988: Becke introduces new numerical implementations, making his test calculations of DFT methods "uncontestable." He also publishes the new DFT functional B88, with gradient corrected exchange, producing better results.

1991: The tipping point?—Becke shows quantum chemists at a conference in Menton, France, that his results by KS-DFT based on the B88 functional with local correlation for atomization energies of a library of molecules rival correlated *ab initio* results of far greater computational costs. Leading quantum chemists (Pople, Handy, and others) accept DFT.

1993: Becke introduces partial exact exchange (hybridization) to achieve even higher accuracy of KS-DFT, e.g., by use of the B3LYP functional.

1998: The Nobel Prize in chemistry goes to W. Kohn for DFT and J. Pople for quantum chemical advances.

2000: DFT is the favored quantum chemical computational method for large molecular systems and continues to be refined by hybridization, application of physical constraints, dispersion corrections, etc. DFT is established in chemistry.

Russell J. Boyd, Dalhousie University, Canada

A Recollection of Axel Becke

I knew Axel many years before he became known to the DFT community. During my four decades as a professor at Dalhousie University, I had the good fortune to work with many brilliant students and colleagues. My curriculum vitae lists 25 completed Ph.D. theses, six MSc theses, and 22 BSc theses. In addition, forty postdoctoral fellows and senior visitors were critical contributors to the research environment. No one in my group had a clearer vision of the research path they intended to pursue than Axel Becke.

My first correspondence with Axel was in the summer of 1980. At the time, he was a Ph.D. student in theoretical physics at McMaster University. His supervisor, Donald W. L. Sprung, an eminent nuclear physicist, granted Axel considerable leeway to set his own course and to explore his own options. Richard Bader served on Axel's advisory committee. Axel met Ziegler, then a postdoctoral fellow with Bader, at a McMaster seminar given by Evert Jan Baerends from Amsterdam. At the time, Baerends and Ziegler were two of the most prominent researchers in the field of Xα computational chemistry and were heavily committed to developing the Amsterdam Density-Functional (ADF) program. This meeting was the beginning of many conversations that were central to Axel's rise to prominence.

As his doctoral research neared completion, he contacted most of the major departments of physics and chemistry in Canada about postdoctoral opportunities. In his letter of July 22, 1980, Axel wrote:

"My research involves the study of local exchange approximations and their application to atomic and molecular systems. To facilitate this study, I have developed a numerical procedure in coordinate space (i.e., no basis sets) for calculating the structure of diatomic molecules. The application of this numerical method and the Hartree–Fock–Slater approximation to selected first row atoms forms the basis of my forthcoming thesis."

In his letter, Axel indicated that he would appreciate the opportunity to continue this work as a postdoctoral fellow and indicated that he intended to apply for a Natural Sciences and Engineering Research Council Postdoctoral Fellowship. Based on his record, it was immediately clear that he would be highly likely to receive the award. I wrote a very positive reply in which I indicated that I would be delighted to have him join us at Dalhousie. I encouraged him to apply for one of Dalhousie's prestigious Killam Postdoctoral Fellowships. With an NSERC or Killam Fellowship, I indicated that I could guarantee him as much freedom as he desired to pursue the application of local exchange approximations to atoms and molecules and related topics. I noted that "our research experiences have been quite different, but I think there is sufficient overlap and complementary interests that we could have a fruitful collaboration. At the same time, I would encourage you to establish yourself as an independent researcher. This is important if you think beyond your postdoctoral fellowship."

While we were waiting for the outcome of his applications for postdoctoral fellowships, I pointed out that I was organizing a symposium on theoretical chemistry in June 1981 at the 64th Canadian Chemical Conference in Halifax. I suggested that he should contribute a paper based on his doctoral research on diatomic molecules. The symposium opened with a keynote paper by John Pople, which was followed by invited papers by Paul Mazey and Vedene Smith. Later in the session, Axel gave a brilliant and lucid lecture that foretold of many more to come. Many people asked me, "Who is that guy?" I detected considerable envy when I told them that he would be joining my group later that summer.

Axel received both his NSERC and his Killam Fellowships and remained at Dalhousie for a third year thanks to an E. B. Eastburn Fellowship. During his three years as a postdoctoral fellow, Axel was always supportive of the other members of the group, but I never pressured him to contribute to any of the projects that were of interest to me at the time. I note with pleasure that his publications from his postdoctoral years (1981–1984) are single-author papers and that he went on to become one of the best theoretical chemists of all time.

A fuller account of Axel's life during the period covered here can be found in his essay, Adventures of a Physicist in the Queen's Chemistry Department: https://www.chem.queensu.ca/sites/chemwww/files/uploaded.files/About/History%at%20Queens//Reminiscences%and%20Recollections%202002.pdf.

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Professor Axel Becke (June 10, 1953–October 23, 2025)—An Appreciation

I revered Professor John C. Slater, having taken his undergraduate course at MIT on the electronic structure of atoms, and subsequently heard many of his more advanced lectures at the Sanibel Island Winter Institute held in January 1968. When Professor Slater visited my advisor, Professor Frank Harris, at Stanford later in the same year, we had some further conversations, and he graciously signed all four of my copies of his legendary electronic structure book series. I am probably a contrarian in thinking that Slater's 1950 paper concerning statistical exchange is the most important paper in what we now call DFT. Reference 8 was published on February 1, 1951, in the Physical Review. My view is that the famous Hohenberg–Kohn paper[6] is largely philosophical, a view shared by Slater. Furthermore, while the Kohn–Sham paper[7] is extremely important, it was a brilliantly imaginative extension of Slater's 1951 paper on statistical exchange. I can imagine John Slater saying with a chuckle, "So, Walter has finally discovered orbitals." However, Slater greatly appreciated the Kohn–Sham paper and used it in his later research.

Although John Slater was my hero, I was disappointed in the work subsequently flowing from his school, which was labeled the X-Alpha method. I concede that my skepticism of X-Alpha was based on personal experience. Keith Johnson (1936–2025), one of Slater's later proteges and, for a time, professor of materials science at MIT, gave an informal seminar at Berkeley, where I was in my second

year as an assistant professor. It seemed to me that Johnson all but claimed he had solved Schrödinger's equation with his latest version of X-Alpha. Using a carefully selected set of chemical examples, Johnson reported remarkable agreement with experiment. Careful reinvestigation of those and related problems subsequently showed that the triumphs of the X-Alpha method were not representative, suggesting a measure of duplicity in the claims of great success. Keith Johnson withdrew from quantum chemistry, retired early from MIT in 1996, and became known as a filmmaker.

In this discussion, I must confess that my career has been devoted to the development and application of convergent quantum mechanical methods. These are methods, such as configuration interaction or coupled cluster, that can be pursued in a logical order to find the exact solution to Schrödinger's equation. Prior to 1980, many quantum chemists thought that Möller–Plesset perturbation theory would be another convergent quantum mechanical method, but later studies showed the MPn series to be highly erratic in terms of energetics. My affection for convergent quantum mechanical methods necessitates that I be at least somewhat skeptical of less direct theoretical methods such as DFT.

Following the Keith Johnson era, some progress was made on theoretical methods related to X-Alpha. Although different scientists were involved, the work of Evert Jan Baerends seemed particularly important to me. The entire field of DFT was turned upside down at the July 1991 International Congress of Quantum Chemistry in Menton, France. The presentation by Axel Becke (Queen's University, Ontario) demonstrated that, with just a few empirical parameters, a reliable DFT method achieved excellent agreement with experiment for a broad range of difficult-to-predict thermochemical energetics. I was not present at the Menton Congress but almost immediately began receiving rave reviews of Becke's research from many sources. The 1991 Becke Menton lecture was of greater influence on chemical theory than any other scientific lecture I can recall.

John Pople and his students Peter Gill and Benny Johnson immediately adopted Becke's new BLYP method and quickly incorporated it into their already popular Gaussian programs. In 1993, Axel Becke introduced his three-parameter hybrid functional B3LYP, and this became a standard in the Gaussian programs. Even as much a "DFT skeptic" as I began encouraging my students to use Becke's B3LYP method to study systems too large for reliable wave function methods. Becke's old B3LYP method is still widely used today and, despite criticism, is still quite useful for the study of certain types of chemical problems.

On Nobel Prize Tuesday, October 13, 1998, I presented the annual Kenneth S. Pitzer Lecture at the University of California at Berkeley. In addition to my prepared lecture, I presented a few observations on the John Pople–Walter Kohn Prize. At the end of my lecture, my colleague and friend, Professor Robert A. ("Bob") Harris, stood up. Bob stated with no hesitation, "If Pople and Kohn deserved the prize, then Axel Becke should have shared it." Wisdom for the ages.

Similar to many others, I became friends with Axel Becke after realizing the profound nature of his contribution to DFT. Axel gave the Annual Robert S. Mulliken Lecture at the University of Georgia in the year 2000 and spent two days with us at the Center for Computational Quantum Chemistry. Axel and I talked for the better part of a day concerning science and other things. He was a real gentleman, and I am thankful to have enjoyed his friendship, however briefly.

I might make one other comment, as we contemplate Becke's research beyond B3LYP. Until his early passing three months ago, Axel Becke continued working on the fundamental understanding of the theoretical foundations of DFT. In my opinion, along with John Perdew, Axel continued to make the most important methodological contributions to the density functional theory.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Sture Nordholm: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Writing – original draft (equal). **Evert Jan Baerends**: Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Kieron Burke**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal)l. **Peter Gill**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Paola Gori-Giorgi**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Stefan Grimme**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Martin Head-Gordon**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Trygve Helgaker**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Erin Johnson**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **Robert O. Jones**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **John Perdew**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Dennis Salahub**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Andreas Savin**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Gustavo Scuseria**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **David J. Tozer**: Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). **Weitao Yang**: Conceptualization (equal); Formal analysis (equal); Investigation (equal);

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DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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