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Obituary: Density Functional Theory (1927–1993)

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Density Functional Theory, or DFT as she is more commonly known, was born during 1927, in the immediate aftermath of the Second Quantum Revolution. By the time of her death, two-thirds of a century later, she had inspired a revolution of her own and had launched the careers and reputations of an entire generation of professors and conference organizers. Although of reputable Anglo–Italian descent,[1] her legitimacy was questioned throughout her life and remains a conversation piece in avant-garde campus cafés.

She entered an uncertain world, rocked by the revelations of Born and Bohr and haunted by the images of half-dead cats conjured up by her older brother, Wavefunction Theory. He seemed able to explain almost everything—from the mind-boggling double-slit experiment to subtle details of molecular structure—but his wisdom often seemed to verge on the mystical. He was particularly fond of swapping identical particles (an annoying habit inherited from his uncle Pauli) and drawing conclusions that baffled those with a classical education. He called his trick 'exchange', a trivial term for a profound phenomenon. His disturbing genius had been recognized while he was still in his infancy and his Nobel Prize, conferred in 1933 when he was only seven years old, lent him a gravitas that was to dominate the relationship with his sister for many years.

They interacted little during their childhood, and notes from the Cambridge Philosophical Society show that, shortly after Hartree and Fock had sketched a self-satisfied caricature[2,3] of her brother, she was adopted[4] by her godfather Dirac. He began to teach her how to mimic her brother's trick but she was too young to do this properly, except when swapping electrons within a completely uniform density. Soon afterwards, perhaps frustrated by her limitations, he abandoned her and, a few years before the outbreak of war, she fell into German hands.

von Weizsäcker rebuked her naïve assumption that all electron densities are uniform, and his insights[5] were a key turning point in her development. However, after correcting her concerning gradients, he too lost interest and went to help Heisenberg to build a bomb. Abandoned once again, and unable to find gainful employment in Europe, she drifted west.

Following the invention of the digital computer during the war, there was interest in the development of computational methods to assess the accuracy of the Hartree–Fock caricature. Difficulties arose, primarily because Fock had ensured that his caricature could still play the exchange game, but Boys, Roothaan and Hall demonstrated[6–8] how these could be overcome. However, in the same year, Slater pointed out[9] that the task becomes very much easier if the subtle exchange game of Wavefunction Theory is replaced by the imitation of his sister. Admittedly, her mimicry was imperfect in non-uniform systems, but the solid-state physicists had convinced themselves that, in metallic systems, the sea of electrons is calm. So, without further ado, they declared her to be a model and embraced her.

The Xα model, as Slater now designated her, was used and exploited by him and others. Despite misguided attempts to make her operate in a muffin tin, her profile quickly rose and she became one of the first supermodels of solid-state physics. Her successes in chemistry and molecular physics, where her assumption of uniformity was manifestly invalid, were less noteworthy, however.

Many young women yearn to be models, and few succeed. Even more rarely, one has the opportunity to become a

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theory. But this is what happened to our heroine when, in 1964, Hohenberg and Kohn proved that, if DFT is dressed correctly, she can yield exactly the same information as her complex older brother, Wavefunction Theory.[10] This was an astonishing discovery, not only because it emphasizes the importance of proper attire, but also because it radically altered the perceived relationship between the siblings. No longer could he claim primacy over his sister; she had become, in very principle, his equal.

This was such an important point that it warrants elaboration. An *n*-electron system has a complex multi-dimensional wavefunction $\Psi\,(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$ that depends on the coordinates of all of its electrons. From such a wavefunction, we can obtain the familiar electron density

$$\rho(\mathbf{r}_1) = n\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)\, d\mathbf{r}_2\, d\mathbf{r}_3 \ldots d\mathbf{r}_n$$

which gives the probability that an electron will be found at the point $\mathbf{r}_1$, by integrating over the coordinates of all but one of the electrons. Remarkably, according to the Hohenberg–Kohn proof, no significant information is lost in this integration and, therefore, the electron density is as fundamental a variable as the original wavefunction. This was the breakthrough that allowed Density Functional models to aspire to the status of theories and earned Walter Kohn a share of the 1998 Nobel Prize for chemistry.

Naturally, there was a catch and it is in the fine print. The Hohenberg–Kohn argument is what mathematicians call an existence proof, as opposed to a constructive proof. That is, although we now know that, *in theory*, DFT can extract as much information from $\rho(\mathbf{r})$ as her brother can from $\Psi\,(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)$, no-one knew how to dress her so that she could achieve this *in practice*. All quantum mechanical theories are created equal, but some are more equal than others.

Thus she entered middle age, outwardly self-confident but inwardly racked by self-doubt. Her admirers—and she had many—extolled her virtues with an evangelical fervour: her detractors—and she had many—attacked her shortcomings with a jealous vigour, rejoicing in her occasional lapses and drawing unfair comparisons with her brother's almost unerring accuracy. In truth, she was neither as virtuous as her supporters claimed, nor as flaky as the Wavefunction aficionados alleged. She occupied an important middle ground, neither as profligate, nor as accurate, as her brother.

But computational scientists make demanding masters and, before long, she was being driven to change. "You would be much more attractive", they whispered, "if you would submit to a little parameterization. It won't hurt very much". Not content with her elegant simplicity, they insisted that she provide the same results as her sophisticated and expensive brother, but at a fraction of his price. Motivated by an insatiable hunger for perfection at no cost, they cared not a whit for her welfare.

So the re-invention began. Layers of parameters—the rouge of computational science—were plastered onto her frail frame until, as the final decade of the century dawned, she could barely recognize herself. "The panacea for all of quantum chemistry's ills!", some declared. "Mutton dressed as lamb", others muttered and, sickened, she silently agreed.

Finally, after suffering from a succession of excruciating fits, she turned to an eminent Canadian surgeon. He examined her, drew a deep breath and sighed. "There is little that I can do for you", he admitted. "You have advanced Hyperparametric Disorder and there is no known cure. You should resign yourself to a future of infinite regression."

"Oh no!", she cried. "The only thing worse than *rigor mortis* is the death of rigour!"

He paused. "There may be another way", he said slowly. "But it is very experimental." She looked up at him but he turned away, unable to face her as he revealed his ghoulish plan. "Shelley has reported[11] that it may be possible to blend the best fragments of two beings into a single, unified organism. The two beings are destroyed in the process, of course, but their glorious synthesis ensures their immortality forever! It's called half-'n'-half theory."

His proposal was now obvious. Her future lay in an abhorrent alliance with her brother and the creation of a grisly hybrid. The concept was as ghastly as it was irresistible and so, in 1993, the surgeon finally released DFT from her parametric prison.[12] To the surprise of many, the operation did not prove fatal to her brother, who continues to flourish in a number of good universities and software packages. Although it was soon discovered that the hybrid had inherited Hyperparametric Disorder from its mother, it has since attained cult status and has a huge following, particularly among organic chemists. It has recently applied to become a religion.

How future generations will remember pure DFT, I cannot say. But, as we reflect on her passing and consider the contribution that she has made to our subject, we may note the following. She was misunderstood and abused, held in naïve awe by some and in contempt by others, capable of stunning successes and dismal failures. Her simplicity was seductive but her flaws ran deep and, in the end, her fall was inevitable. But, above all, she was elegant and there is little more that one can ask of a scientific theory.

She is survived by her older brother, her dubious offspring and a number of poor relations, including Molecular Mechanics, Hückel Theory, and Chemical Intuition.

References

[1] L. H. Thomas, *Proc. Cambridge Philos. Soc.* **1927**, *23*, 542; E. Fermi, *Rend. Accad. Naz. Lincei* **1927**, *6*, 602.
[2] D. R. Hartree, *Proc. Cambridge Philos. Soc.* **1928**, *24*, 89.
[3] V. Fock, *Z. Phys.* **1930**, *61*, 126.
[4] P. A. M. Dirac, *Proc. Cambridge Philos. Soc.* **1930**, *26*, 376.
[5] C. F. von Weizsäcker, *Z. Phys.* **1935**, *96*, 431.
[6] S. F. Boys, *Proc. R. Soc. London, Ser. A* **1950**, *200*, 542.
[7] C. C. J. Roothaan, *Rev. Mod. Phys.* **1951**, *23*, 69.
[8] G. G. Hall, *Proc. R. Soc. London, Ser. A* **1951**, *205*, 541.
[9] J. C. Slater, *Phys. Rev.* **1951**, *81*, 385.
[10] P. Hohenberg, W. Kohn, *Phys. Rev. B* **1964**, *136*, 864.
[11] M. W. Shelley, *Frankenstein* **1818** (Lackington, Hughes, Harding, Mavor and Jones: U.K.).
[12] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372.