

Perspective

Perspective on “Density functional thermochemistry. III. The role of exact exchange”

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Abstract. Recent developments in density functional theory have transformed the entire field of quantum chemistry. This paper provides a perspective on Becke’s landmark papers in 1992 and 1993 that led to the popular density functionals such as B3LYP.

Key words: Quantum chemistry – Density functional theory – Theoretical thermochemistry

One of the most dramatic changes in the standard theoretical model used most widely in quantum chemistry occurred in the early 1990s. Until then, *ab initio* quantum chemical applications [1] typically used a Hartree–Fock (HF) starting point, followed in many cases by second-order Møller–Plesset perturbation theory. For small molecules requiring more accuracy, additional calculations were performed with coupled-cluster theory, quadratic configuration interaction, or related methods. While these techniques are still used widely, a substantial majority of the papers being published today are based on applications of density functional theory (DFT) [2]. Almost universally, the researchers use a functional due to Becke, whose papers in 1992 and 1993 contributed to this remarkable transformation that changed the entire landscape of quantum chemistry.

DFT within the local density approximation (LDA) has been used extensively for decades in computational physics; however, its deficiencies, such as the substantial overestimation of molecular binding energies, were well known. Consequently, applications using LDA for molecular systems [3] were limited, particularly relative to the large number of quantum chemical studies using HF-based methods. The emergence of gradient-corrected density functionals in the late 1980s increased the accuracy of such methods significantly. Becke proposed one of the most successful gradient-corrected exchange functionals (B88) in 1988 [4]. Used in conjunction with

gradient-corrected correlation functionals such as those of Perdew (P86) [5], Lee, Yang, and Parr (LYP) [6], or Perdew and Wang (PW91) [7], density functional methods were successfully used in many applications [8]; however, these important developments did not initially have much impact on the mainstream *ab initio* quantum chemistry community.

It was at this juncture that Becke started a series of publications on “Density functional thermochemistry” [9–13]. The title publication on the “role of exact exchange” is the third paper in this series [11] and has had an astonishing impact on the entire field of quantum chemistry. One clear measure of the impact of this 1993 paper is that it has already accumulated more than 2200 citations in the scientific literature in less than 6 years [14]. Interestingly, most of the citations are from practitioners of quantum chemistry who have investigated a variety of chemical applications using functionals such as B3LYP with commercial software packages.

One of the most important reasons for the impact of Becke’s papers was his decision to assess the DFT methods systematically on the same set of test molecules assembled by Pople and coworkers in their development of the Gaussian-*n* methods [15–18]. The successful G1 [15, 16] and G2 [17] methods were the first two methods developed for the prediction of the thermochemistry of small molecules within chemical accuracy (± 2 kcal/mol). In order to assess the performance of these theoretical methods, Pople and coworkers also developed a set of test molecules for which accurate experimental thermochemical information is known. Becke adopted the initial G1 test set containing 55 neutral molecules as the standard test set for the development and assessment of new density functionals. This immediately provided a mechanism for an unbiased comparison of the performance of DFT methods with the state-of-the-art *ab initio* quantum chemical techniques for the same set of molecules.

The first two papers in the series by Becke [9, 10] explored the improvement in the predicted thermochemistry of DFT methods due to the inclusion of gradient corrections from exchange (B88) and correlation

(PW91), respectively. While the PW91 correlation had only a small effect, the inclusion of B88 exchange caused a dramatic improvement. The mean absolute deviation for the calculated dissociation energies of 55 molecules in the G1 test set decreased from 36.2 kcal/mol (LDA) to 3.7 kcal/mol (B88). For comparison, the state-of-the-art G2 method had a deviation of 1.2 kcal/mol [17]. Becke presented these results at the 7th International Congress in Quantum Chemistry at Menton, France, in July 1991. The performance of the B88 functional was even more remarkable for a method that is no more expensive computationally than HF theory. The implications for larger molecules and for the future of quantum chemistry were obvious.

Becke's initial papers immediately caught the attention of the mainstream *ab initio* quantum chemistry community. In particular, Pople and coworkers started to investigate gradient-corrected density functional methods. Even more importantly, they were quickly able to implement them efficiently in the Gaussian 92 computer program [19]. In fact, their implementation included a fully self-consistent solution of the Kohn–Sham equations for the available gradient-corrected density functionals. This was an improvement over Becke's original implementation, which was only post-LDA (self-consistent treatment at the LDA level followed by evaluation of the functional using LDA densities). Pople presented a preliminary assessment of the applicability of DFT methods at the Sanibel quantum chemistry symposium in 1992 [20]. The widespread availability of the Gaussian program coupled with Pople's influence resulted in a large number of quantum chemists starting to use DFT methods. Interestingly, Pople and coworkers performed most of their initial assessment [21, 22] using the BLYP functional (B88 exchange and LYP correlation) which immediately became one of the most popular density functionals.

The third paper by Becke [11] was published at this point and introduced a key theoretical concept – the role of exact exchange. In an earlier paper, Becke had used ideas from the “adiabatic connection” formula to show that a novel “half-and-half” mixing of exact exchange energy (as evaluated in HF theory) with that from LDA yielded improved results [23]. The title paper explored this idea further and concluded that exact exchange must play a role in highly accurate density functional methods. In addition, Becke introduced a semiempirical generalization to determine the extent of mixing of exact exchange based on fitting to the G1 thermochemical data. In fact, he proposed the following formula containing three different semiempirical parameters:

$$E_{xc} = E_{xc}^{LDA} + a_0(E_x^{\text{exact}} - E_x^{LDA}) + a_x \Delta E_x^{B88} + a_c \Delta E_c^{PW91} .$$

The semiempirical coefficient a_0 determines the extent of replacement of electron-gas exchange with exact exchange, and a_x and a_c determine the optimum inclusion of gradient-correction for exchange (B88) and correlation (PW91), respectively. Becke determined the coefficients by a linear least-squares fit to 56 atomization energies (the original 55 molecules + H₂), 42 ionization

potentials, and 8 proton affinities in the G1 test set along with 10 first-row atomic energies to get $a_0 = 0.20$, $a_x = 0.72$, and $a_c = 0.81$. Using the three-parameter fit, Becke obtained a mean absolute deviation of 2.4 kcal/mol for the atomization energies of the molecules in the G1 test set. This was only a factor of 2 from that of G2 theory (1.2 kcal/mol) and very close to the target value of ± 2 kcal/mol to reach chemical accuracy.

There are several interesting points to note about this expression proposed by Becke. First of all, the use of a small number of semiempirical parameters obtained by fitting to the G1 test set is somewhat reminiscent of the parameters (“higher-level corrections”) used by Pople and coworkers in their formulations of the Gaussian-*n* methods [15–18]. More interestingly, in today's notation, Becke's functional as defined above is represented as B3PW91, where B3 refers to the three parameters in the defining expression and PW91 refers to the correlation functional used. The functional B3LYP that is most popular in the quantum chemical literature today uses LYP instead of PW91. Becke never did propose or endorse the use of the B3LYP functional; however, the Gaussian 94 program [24] allowed the use of different combinations of exchange and correlation functionals and included an implementation of the B3LYP functional (with an easy-to-use keyword). As defined, the B3LYP functional uses the same semiempirical parameters derived by Becke (for B3PW91) without any re-optimization. Nevertheless, B3LYP appears to perform somewhat better than B3PW91 in careful assessments. For example, in a recent critical evaluation of seven different density functionals, B3LYP had the lowest mean absolute deviation from experiment for the heats of formation of 148 molecules in the G2 test set [25]. Surprisingly, refitting of the three parameters in the B3LYP functional yields only a slight improvement.

Overall, Becke's landmark series of papers were the key ingredients in causing an important transformation in quantum chemistry. The first two papers were instrumental in getting the attention of the *ab initio* quantum chemistry community, while the third paper provided the key idea of the role of exact exchange that led to the highly successful functionals such as B3LYP. Interestingly, the need to evaluate explicit exchange integrals has made it difficult to incorporate such functionals in the conventional software packages used by the computational physics community; however, the quantum chemistry community has embraced this approach that has led to a dramatic increase in the number of users and applications using such hybrid density functionals. The powerful DFT methods are now an essential part of the arsenal of computational quantum chemistry.

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