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Perspective

From Xα-scattered wave to end-of-the-century applications of density functional theory in chemistry. Perspective on "Chemical bonding of a molecular transition-metal ion in a crystalline environment"

Johnson KH, Smith FC Jr (1972) Phys Rev B 5: 831–843

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Abstract. The paper by Johnson and Smith is representative of the Xα -scattered wave (SW) effort of the 1970s. Despite the severe approximations that were necessary at the time, the paper shows that a "first-principles" Xα calculation yields a compelling account of the electronic structure and spectrum of permanganate. Contemporaneous semiempirical and ab initio calculations were not up to the task. The quality of the results and the prospect of treating really large systems were sufficient to attract the attention of many quantum chemists (as well as the disdain of some and the ire of others). The Xα-SW work was an important link in the chain of contributions that would bring density functional theory into chemistry.

1 am.

A faint knock on the downstairs door. Or was it?

Then the unmistakable thump of a heavy boot against the door and the crack of the door jam as it shattered.

Had his sordid past caught up with him? The interrogation would be swift and on the spot. Where did that wooden chair come from? And the bare light bulb slowly swaying above it? Whose face was that, almost invisible behind the glare?

Inquisitor: Are you now or have you ever been a member of the Xα party?

Mild-mannered respectable density functional theory practitioner (MMRDFTP): What? (Where had he heard that voice before?)

Inquisitor: Are you now or have you ever been a member of the Xα party?

MMRDFTP: I'm a Mild-mannered respectable density functional theory practitioner (MMRDFTP). What do you mean by breaking into my house in the middle of the night and hauling me out of bed like that? I was just in the middle of a great dream about an exchange–correlation functional that had the right asymptotic form and took care of dispersion seamlessly. Could have done excited states too… and eminently parallelizable. And now I've forgotten what it looked like…

Inquisitor: Answer the question or you'll be eating your teeth for breakfast. Are you now or have you ever been a member of the Xα party?

MMRDFTP: OK, OK, I did do some Xα calculations a long time ago. But only a few…

Inquisitor: Why'd ya do it?

MMRDFTP: Desperation I guess. We wanted to do transition metals and then really complex systems. The semiempirical methods could only go so far and Hartree–Fock… Well, life is short… So when we heard about the Xα stuff we had to have a close look. The great physicist John Slater was pushing Xα. Slater [1] had proposed his approximate "statistical" treatment of exchange to be able to treat larger systems. Keith Johnson in his group adapted one of the solid-state band techniques (the Korringa–Kohn–Rostoker method [2, 3] – yes, the Kohn is the DFT Kohn…) to use nonperiodic, molecular, boundary conditions, the Xα-scattered wave (SW) method. This involved some pretty drastic approximations for the one-electron potential (the Kohn-Sham [4] potential in modern language, though Slater wasn't thinking in terms of a potential that included correlation – to him, Xα was derived by introducing approximations into the Hartree–Fock equations [5]). In the Xα-SW method one built spheres around each of the atoms and took a spherical average of the potential in them. Between the spheres, for want of anything better, a constant average potential was used. If you make a

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picture it looks like round wells around the atoms with flat areas in-between. Hence the name muffin-tin potential. Some of the quantum chemists took great joy in making fun of it – the Rin-Tin-Tin potential… etc. It was a pretty ugly potential… Actually, some of the discussions were pretty ugly too, but I digress… The muffin-tin approach had some advantages too. You didn't have to optimize basis functions, in a sense the molecule did it for you. It was fast, infinitely fast in comparison to post-Hartree–Fock methods. And in the end, the results were good enough to solve a lot of problems, but of course not everything.

Inquisitor: OK, enough blah-blah. What kind of problems could you solve with Xα?

MMRDFTP: Like I said, transition metals and the like. Things that just seemed hopeless with other methods. No one was thinking in terms of organic chemistry or 2 kcal/mol or anything like that at the time, the way you can with modern DFT. In retrospect, neither the functionals nor the techniques for solving the Kohn–Sham equations were ready yet. That would take a few more years. The 1972 paper of Johnson and Smith [6] on permanganate is a good example. For transition metals, even seemingly simple complexes such as MnO_4^- present a formidable correlation problem. Hartree–Fock calculations were just too far off the mark to be realistic. So if one needed to understand such systems through quantum chemistry, it was pretty desperate, either semiempirical or Xα. Johnson and Smith did an Xα calculation, including the effects of the surrounding crystal in a rough manner (a positively charged sphere surrounding the whole permanganate anion to stabilize it) and gave a detailed analysis of the spectrum and the orbitals. They were very much concerned with being able to treat even more complex systems, impurities in solids, enzymes and the like, just the systems where modern DFT is showing such promise.

Inquisitor: You're making it all sound too rosy. There's no real link between Xα and muffin tins and all that and real legitimate DFT calculations.

MMRDFTP: "Legitimate DFT"…interesting… Actually, there are several links, a whole chain, in terms of getting DFT into better shape and into quantum chemistry. In the Florida school there were several attempts to get rid of the worst features of the muffin-tin potential but none of them were really successful. Then Dunlap, Connolly and Sabin [7] made a great contribution. Building on previous work of Sambe and Felton [8], they formulated a linear combination of atomic orbitals-Xα method using Gaussian orbitals and fitting functions for the Coulomb and exchange–correlation terms. Dunlap's program inspired others, such as deMon and DGauss. In parallel, the so-called discrete variational method [9] spawned modern codes, such as DMol and ADF. Then when the functionals got good enough to get DFT into Gaussian and the other mainstream quantum chemistry codes it all became very respectable. So can I go back to sleep now?

Inquisitor: Not quite yet, I want to ask you a question about your use of cluster models…

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