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This Week's Citation Classic

Desclaux J P. Relativistic Dirac-Fock expectation values for atoms with Z = l to Z=120. *Atom. Data Nucl. Data Tables* **12**:311-406, 1973. [Centre d'Études de Limeil, Villeneuve St.-Georges, France]

This compilation provides a systematic comparison between relativistic and nonrelativistic Hartree-Fock results for all the neutral atoms of the periodic table and enables one to decide when relativistic corrections need to be included in a realistic calculation of electronic properties. [The *SCI*® indicates that this paper has been cited over 140 times since 1973.]

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"About 20 years ago any theoretician involved in atomic calculations had a rather pleasant job since any disagreement between experimental results and his calculated values was immediately and 'obviously' attributed to correlation and/or relativistic corrections. With the growth in the 1960s of various methods to handle the many body problem, the only magic word left to explain discrepancies was relativity. About that time, I started worrying with a few other physicists about how we could practically calculate these corrections. I don't think that it was a very original idea but it was just the right time to consider this problem. First, as stated above, it was, at least in atomic physics, the next obvious correction to be included. Second, progress in computers made it possible to carry out reliable estimates even for heavy atoms. It was still the time when almost everyone believed that relativity would modify in a sizeable way only the calculated properties of core electrons in heavy atoms, the only ones to have a mean velocity not too small compared with the speed of light Some clever people already had the feeling that these corrections would also be important for valence electrons at least for the properties involving their wavefunctions in the vicinity of the nucleus, and this is how I got the subject of my PhD work: influence of relativistic corrections on hyperfine structure constants.

"I thus started to develop a relativistic Dirac-Fock program and when the first results came out, I was more than surprised by some of them which showed that, in terms of percentage, the relativistic corrections were sometimes more important for valence electrons than for core ones. At first I thought that something was going crazy in my code, but after comparing results with D.F. Mayers and later with J.B. Mann, I had to admit that I must reconsider my simple-minded view of relativistic corrections. This unexpected behaviour, at least for me (and at that time I don't think that I was the only one, even if nowadays some people claim it is obvious, obvious when you know the answer of course!), prompted me to do a more systematic investigation throughout the periodic table by comparing relativistic and nonrelativistic results for all the neutral atoms. The next problem was to put all this information into a suitable form for publication. Being lazy, I would certainly never have reached this point if some friends had not urged me to do so.

"I am more than pleased to learn that this compilation has been cited so often. One reason is that until recently it remained the only one to provide a systematic estimate of relativistic corrections along the periodic table. Another is that it may have helped to popularize the idea that for valence electrons of medium and high Z atoms, the relativistic corrections cannot be ignored and are in fact of some importance even to interpret chemical properties.[1] But the main reason is certainly that the timing was just right when it was published."

1. **Pyykkö P & Desclaux J P.** Relativity and the periodic system of elements. *Account. Chem. Res.* **12**:276-81, 1979.