CAT(computer-aided thinking) in chemistry

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The first concerted effort of advancing computational chemistry was put forward at Mulliken's laboratory in the Department of Physics at the University of Chicago. It was late 1950s. Drawing inspiration and substantial benefits from Kotani's Table of molecular integrals, Ruedenberg and Roothaan prepared a general mathematical algorism for the calculation of one- and two-center molecular integrals over STOs. Then, led by Roothaan, a bunch of young people, including Bagus, Clementi, Fraga, Kolos, McLean, Moccia, Ransil, Wahl, Weiss, and Yoshimine, developed a system of computer programs for diatomic molecules at the level of the SCF approximation. For the program debugging and also for the production runs, they were flying back and forth between Chicago and Dayton, Ohio. I joined them in 1958 as a research associate. They were using the UNIVAC computers housed in a large building inside the Wright-Patterson Air Force Base in Dayton. Roothaan was certainly a driving force behind the molecular computational project but every one in the bunch, sometimes called the Chicago Gang, was driven by one's own dream and passion to open a new chapter of the computational chemistry. The entire harvest reaped by UNIVAC was vast and extensive, including Kolos' historic work on the hydrogen molecule. The totality of their achievement was truly amazing if one thinks of the fact that computers available to the Chicago Gang in those days were incomparably inferior to today's personal computers any school kid can lay his/her hands on, both in terms of speed and in terms of memory capacity.

There was, however, a severe deadlock for the Chicago project. The problem was in the choice of STOs as the expansion basis functions. Computations of 3- and 4-center molecular integrals over STOs are extremely difficult and that implied virtual impossibility of extending molecular computations to chemically interesting molecular systems, including all organic substances and metallic complexes. The only hope appeared to be in the switching of basis set choice from STOs to GTOs. In 1964 I embarked in earnest on the preparation of GTO basis sets usable for high quality multi-center molecular calculations.

In 1968 I started giving a quantum chemistry course at the University of Alberta in Canada. Soon after that, in 1970, came out that little book entitled "The conservation of orbital symmetry" by Woodward and Hoffmann. The book was a lucid presentation of the Woodward-Hoffmann rules. The publication caused a commotion among organic chemists in the Department of Chemistry. One day a senior member of the Organic Division walked into my office and said to me, "We don't need anymore to grapple with quantum mechanics. All we need is to learn the Woodward-Hoffmann theory." Quite probably he meant it as he spoke firmly albeit jokingly.

I did not flinch and countered that organic chemists need to learn more quantum mechanics, not less, now that the Fukui-Woodward-Hoffmann theory has spectacularly demonstrated, for the first time, that the wave function ϕ itself matters, not indirectly through the electron density $|\phi|^2$. I still think that what I said was right. My only regret is that I could not convince them of the real usefulness of quantum mechanical computation in order to speculate or to analyze the reaction mechanism of organic molecular system.

In the same department Professor Satoru Masamune was making an all-out effort to synthesize cyclobutadiene. It was a difficult work and I tried my best to offer some theoretical support but in those days the computational resources available to me was not powerful enough to render him any meaningful help, even for such a small molecule as cyclobutadiene.

Around 1990 I was toying with the notion of computer-aided thinking in chemistry. The acronym CAT is an obvious imitation of CAD (computer-aided design) widely used in various industrial design works. Imagine an office-desk size computer sitting in an individual research laboratory. The computer consists of hard-, firm-, and softwares specially designed to be dedicated to CAT in chemistry and material sciences. Needless to say, it should be equipped with user-friendly input format and convenient graphic output facilities.

According to what I have learned about a very promising developmental project called EAPC (Embedded High Performance Computing system) project, the dream of CAT may come true sooner than we expect. The project is aptly described in the following paper: "Development of Special Purpose Computers for Various Kinds of Chemical Simulations" by Nagashima, Sasaki, Ohtani, Uehara, Tsukada and Murakami in J. Comput. Chem. Jpn., Vol 4, No 4 (2005), 131. By the very nature of the project, it is absolutely essential

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to keep the project robust for a long period of time.

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