COMPUTATION SPACE

Computational Chemistry as a field has by now developed sufficiently for us to give some rule-of-thumb definition of the 'problem space' within which we, as a discipline, need to operate in order to make useful contributions to the business of chemistry.

In the course of many communications, it has become clear to me that if we had software capable of doing calculations on molecular structures containing perhaps 3000 atoms we would be in fairly good shape—at least for the near term.

In addition to structures of this size, it seems highly desirable (if not mandatory) for such software to be capable of dealing with atomic species up through at least atomic number 80.

Given such a wish list, it is useful to determine where we presently stand.

For example, some very large molecular mechanics calculations using MM2(87) are now being done, some of which I am personally aware have exceeded the 3000-atom limit. These calculations are, however, limited to atomic numbers of no more than 19 or 20, due to the parameter problem which one confronts with such systems.

Further, if one looks at the Ab Initio computational systems (which conceptually would seem to be the most general), one comes to the unhappy realization that reliable basis sets for atoms of higher numbers than 20 are not always readily available nor thoroughly tested and that computations on molecular structures of even 50 atoms are beyond the computer hardware currently available or, indeed, even in the planning stage.

Semiempirical calculations such as MOPAC enable people to carry out 500-atom calculations, but once again a lack of parameters limits one to species of no more than about 20 in atomic number. There is, in fact, a more serious limitation in MOPAC which prevents the easy development of higher parameters—MOPAC uses only *s* and *p* orbitals. The large atomic numbers will most certainly require the addition of *d* orbitals.

Indeed, we have at our disposal only one system—the Extended Hückel approximation—which meets the requirements of being able to handle both large molecular structures and high atomic numbers. The EHT systems offered by QCPE are still heavily requested, thanks to this unique capability. However, these systems as they are presently constituted will not optimize geometries.

The preceding statement has, admittedly, a caveat. There *are* now systems running which do optimize geometries within this approximation, but they are still research vehicles and are not yet publicly available. QCPE is not yet able to make one routinely available.

We find ourselves on the verge of a great era—but we aren't there yet. The geometry-optimizing EHT systems will eventually make a significant contribution, but the quality of their results can be no better than the quality of the approximation itself.

We may have to develop versions of molecular mechanics and systems of parameters which may not be as high in quality as we could hope for but which would let us do high atomic-number

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calculations. This is mere speculation at this point; no large amount of pertinent work is now under way.

One opportunity does exist, and it could be well within our immediate grasp. A major limiting factor on the expandability of the MOPAC system is its lack of *d* orbitals. To date, it has been possible to avoid the *d*-orbital problem by a judicious choice of atom types for which one develops parameters. Obviously this approach will not always be possible, as we are all aware that *d* orbitals play a vital role in chemically critical situations.

Given that a version of MOPAC incorporating a *d*-orbital capability can be brought about by its author, we could find ourselves with two versions of the system: One version would be extensively parameterized, with the other less parameterized (probably a faster version) for systems not requiring *d* orbitals.

There will be no simple or single strategy for bringing computational chemistry up to the stage in which it can routinely handle structures of 3000 atoms and atom species up to atomic number 80, but for computational chemistry to be a useful tool for modern chemistry it must be done.

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