WHEN IS AN ANSWER THE ANSWER?

This question is probably the most puzzling aspect of computational chemistry for the newcomer. A computer program with which one is unfamiliar prints a number on a piece of paper or on a computer screen and it really means very little until one confronts some experiment in which this number, or perhaps a set of numbers, will be given the 'smoke' test. Here the use of this colloquial term may be more appropriate than one might expect as chemistry experiments often involve smoke and a certain amount of noise.

There is the story which I have yet to verify of the graduate student who was supposed to synthesize a series of compounds. The instructions that were given were to first run some calculational system and look at the total energy for the molecule. If the total energy was negative the student could go ahead and make the molecule. If the total energy came out positive the student was to avoid this molecule as this was an indication that it would not be stable. The student dutifully followed the rules and things went along rather well until suddenly the laboratory was shaken by a small explosion which rearranged some of the student's equipment. Fortunately no one was hurt.

The research supervisor rushed in to find out what had happened. The student dutifully produced a printout showing that the molecule should indeed have been stable. In fact, according to the printout it should have been stable by one half of a kilocalorie. The error in the approximation being used in the calculation was on the order of 3–5 kilocal for a typical small molecule. In this case, this answer clearly was not the answer. The message, however, is clear. One needs to have a very precise idea about the error in a typical calculation which one is doing or one needs to have done so many calculations that instinctively an answer of one half of a kilocalorie would have been suspect. Admittedly it takes quite a bit of time to come to this level of familiarity.

There are many people who feel uncomfortable with semiempirical calculations for the type of reason just described. As often as not their answer to this problem is to attempt to use calculational techniques which are 'exact'. They attempt to use ab initio techniques with the largest possible basis set they can afford to run – their thinking being that they can hardly lose since ab initio techniques are exact, or at least begin to approach exact in some manner.

Unfortunately there is a fatal flaw in their reasoning. The culprit in this case is a mathematical fact of life called basis set truncation error.

What we all tend to forget is that in solving the Schrödinger equation we are really solving a differential equation. We are attempting to use some linear combination of a closed set of functions which is to approximate the real solution that probably can not be represented in closed form. To represent the true answer we would need a linear combination of an infinite number of the functions from this set for purely mathematical reasons. Computationally we can not afford to use such a basis set so we truncate it. We cut the linear combination off at some arbitrary number of terms such as six. The error which we introduce by this practice is known as basis set truncation error. In ab initio computations, basis sets such as the STO-3G, which everyone is familiar with, are highly truncated basis sets. A basis set such as 6-31G is certainly better but still truncated and very possibly by a significant amount. I say very possibly because one has no real way of knowing

just how much truncation error one is actually working with. The more truncation error one has the worse the answer is, of course, going to be.

Let us assume for the sake of discussion that one has chosen to use the 6-31G basis set in order to get the best possible answer in a reasonable amount of time. Let us assume that, as in the example above, a series of compounds is being calculated and that for the first five being calculated we have been fairly accurately predictive. This being the case, one has no guarantee that the sixth structure will be as accurate. The reason for this is that while the basis set truncation error for the first five molecules may have been rather similar one has no guarantee that it will be the same for the sixth molecule using exactly the same basis set. Basis set truncation error for a given basis set varies with the structure being calculated and not with the the basis set being used. Once again there is the question about when is an answer the answer.

Yet another instance of this question occurs when someone converts a calculation from one computer to another. This is a practice which appears to be going on constantly and is certainly worth mentioning.

Let us assume that we have a MOPAC-like calculation which was written for a CRAY computer and was being converted to some workstation such as a SUN. When the work is finally completed and comparisons are made it is found that in the case of all structures which are calculated certain important numbers such as the heats of formation are not exactly the same. Is the conversion correct? For example, let us suppose that the CRAY version give a heat of formation of -5.01 kcal and that the converted version gives a heat of formation of -4.96 kcal.

Everyone who has worked with such conversions is aware that digit for digit comparability is not going to be found. The sources of these differences are many. In the first place it must be remembered that the CRAY has a 64-bit architecture and the SUN has really a 32-bit architecture. In the SUN version everything had to be converted to double precision numbers in order to even attempt to be comparable because of the architecture differences. If one fails to recognize this problem the SUN results may be wildly different for numerical reasons. Another source of differences in such conversions is that these computers may be using round-off procedures which are completely different. It should also not be forgotten that all the library routines supplied by the system to calculate values of functions such as sines, cosines and exponentials are numerical approximations and will certainly be different. Given the many potential sources of difference the above answers are probably the same answer from the physics point of view.

The real criterion to apply is that of 'physical reasonableness'. For example, if long experience with a calculational system tells us that its answers tend to have an error of from 2–4 kcal in energy variables then the two answers above certainly agree to within this error. One can next check the details of the wave function and charge distribution on individual atoms. If reasonable agreement is found then the conversion is probably valid. In this case an answer was the answer.

The answer to the initial question is that there is no magic rule which can guarantee that an answer is correct. The fact that this is so continues to justify providing employment for needy chemists and their accumulated wisdom which comes from working in the field.

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