Editorial Note - The People Criteria: Essential and Desirable Features of Model Chemistries

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Editorial Note

The theoretical philosophy that underlies the Gaussian program is based on the concept of model chemistries, formulated by John People. It is characterized by the following principle:

Model chemistry should be uniformly applicable to molecular systems of any size and type, up to a maximum size determined only by the practical availability of computer resources.

This is in contrast to the view which holds that the most accurate modeling method which is practical ought to be used for any given molecular system. However, using different model chemistries for different sized molecules makes comparing results among systems unreliable.

The principle has several implications:

A model chemistry should be uniquely defined for any given configuration of nuclei and electrons. This means that specifying a molecular structure is all that is required to produce an approximate solution to the Schrodinger equation; no other parameters are needed to specify the problem or its solution.

A model chemistry ought to be unbiased. It should rely on no presuppositions about molecular structure or chemical processed which would make it inapplicable to classes of systems or phenomena where these assumptions did not apply.

Once model chemistry has been defined and implemented, it should be systematically tested on a variety of chemical systems, and its results should be compared to known experimental values. Once it demonstrates that it can reproduce experimental results, it can be used to predict properties of systems for which no data exist.

Other desirable features of model chemistry include:

Size consistency/extensively: The results given for a system of molecules infinitely separated from one another ought to equal the sum of the results obtained for each individual molecule calculated separately. Another way of describing this requirement is that the error in the predictions of any method should scale roughly in proportion to the size of the molecule. When size consistency does not hold, comparing the properties of molecules of different sizes will not result in quantitatively meaningful differences.

Reproducing the exact solution for the relevant n- electron problem: a method ought to yield the same results as the exact solution to the Schrodinger equation to the greatest extent possible. What this means specifically depends on the theory underlying the method. For example, Hartree-Fock theory should be- and is able to reproduce the exact solution to the one electron problem; it can treat cases like H^{2+} and HeH+ essentially exactly.

Higher order methods similarly ought to reproduce the exact solution to their corresponding problem. Methods including double excitations ought to reproduce the exact solution to the two- electron problem, methods including triple excitations, like CCSD (T), ought to reproduce the exact solution to the three- electron problem, and so on.

Variation: The energies predicted by a method ought to be an upper bound to the real energy resulting from the exact solution of the Schrodinger equation.

Efficient: Calculations with a method ought to be practical with existing computer technology.

Accurate: Ideally, a method ought to produce highly accurate quantitative results. Minimally, a method should predict qualitative trends in molecular properties for groups of molecular systems.

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