AM1 vs. PM3

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Netters,
    A few weeks ago, Jeffrey Nauss asked about a comparison between the AM1 and
PM3 semiempirical methods.  Both of these semiempirical methods are
included in most programs that support semiempirical calculations (AMPAC,
MOPAC, etc.).  Please note that the following discussion is MY OPINION and
a compendium of MY EXPERIENCES.  I hope you find it somewhat useful.
    The lead references to each method follows:
AM1: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J.
        P. J. Am. Chem. Soc. 1985, 107, 3902.
PM3: Stewart, J. J. P. J. Comput. Chem. 1989, 10, 209.
    AM1 stands for "Austin Model 1" and PM3 stands for
"Parameterization
Method 3".  Both methods implement the same basic NDDO theory pioneered
by Michael Dewar while at the University of Texas at Austin.  The differ-
erence is in how the parameters that the semiempirical methods utilize to
replace portions of the full ab initio implementation of Hartree-Fock theory.
    Perhaps the most important difference between AM1 and PM3 is the
involvement of the researcher in the parameterization process.  PM3 was
developed using a largely undirected mathematical optimization process
with greatly reduced guidance from chemical knowledge or intuition,  an
addition that the Dewar methods consider essential.  The human
researcher knows for which molecules it is necessary to obtain the best fit.
For instance, it is useless to obtain parameters for carbon and hydrogen that
describe the properties of cubane correctly if the results for benzene are
significantly different from experiment.  An attentive and knowledgeable
chemist can also guide the search into areas of the parameter hypersurface
that make sense as far as the absolute magnitude of the parameters themselves
are concerned.  As with many chemical properties, the parameter values should
vary periodically.  While this should not unduly constrain the final values,
parameters should follow well-defined general trends for proper interaction
with other elements.
    In terms of the actual NDDO model, the actual parameters allowed to vary
in the two methods are quite different.  In AM1, a large number of values we
used from spectroscopy for some of the one-center terms and the other
parameters derived with these values fixed.  (This is possible only for the
lighter elements in the Main Group.)  PM3 allowed ALL of these values to float,
resulting in substantially more parameters.
    AM1 also had a quite different concept as to the application of the
Guassian functions introduced with AM1 to adjust the core-electron/core-
electron repulsion function.  Workers in the Dewar group and subsequently in my
group see Gaussian functions as PATCHES to the theory, not integral parts.  All
models fail at some point and the Gaussians were introduced to help with some
of the systematic errors in MNDO.  Traditionally, these patches were applied to
adjust for difficult molecular systems AFTER semiempirical parameters were
stabilized.  PM3 includes these Gaussian functions (two for each element) FROM
THE BEGINNING.  Our experience indicates that in such a situtaion, the
chemistry os the element will very likely be very strongly effected by the
presence of these functions and the importance of the "real",
"chemical"
parameters will be reduced and swallowed up bu the Gaussians.   In short,
Gaussians should only be used where absolutely needed, and then viewed with
askance.
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        The essence of the difference between the two philosophies is evident:
the theoretical basis for the method is either accepted or denied. Significant
approximations are made to gain the speed advantage that semiempirical methods
enjoy over their ab initio quantum mechanical brethren. But both the ab initio
and semiempirical models are based on the Hartree-Fock set of ideas. These
ideas possess theoretical rigor as regards solution of the Schrodinger
Equation. If one simply views the semiempirical parameters as adjustables
within a curve-fit scheme rather than as components of a theoretical model,
little faith or importance resides in the meaning of their final values.
Simply put, the method of parameterization described above and used so
successfully with AM1 and MNDO (and now SAM1) expresses confidence in the
theory. With a firmer footing in chemical reality, AM1 parameters are
more likely to yield useful results for situations not specifically included
in the molecular basis set for parameterization (MBSP).
                        Some Practical Considerations

   The differences in errors between the two methods as published are
minimal, but that does not relate the real story of how the methods perform
differently. Some key points:
   - PM3 is clearly better for NO2 compounds as a larger number of these
        were included in the MBSP.
   - PM3 is usually a little better for geometries, as these were also
        heavily weighted.
   - The molecular orbital picture with PM3 is usually different from that
        expected or that predicted by other methods. This is a direct consequence
        of the lack of attention paid to the absolute values of Uss and Upp.
        It can be seen in the lack of performance in ionization potentials.
   - PM3 charges are usually unreliable, again a result of the rather strange
        values that some of the parameters take on, even when other experimental
        data such as heats of formation and geometries are acceptable. This
        makes PM3 essentially useless for the derivation of molecular m echanics
        force fields. Perhaps the best known example of this is the case of
        formamide. The partial charges for the atoms in the molecules are listed
        below. The lack of any appreciable charge on N has led to a reversal of
        the actual bond dipole between C and N in this molecule!

          Atom   AM1   PM3   HF/6-31G*

           O   -0.3706   -0.3692   -0.5541
           C   0.2575   0.2141   0.5079
           N   -0.4483   -0.0311   -0.8835
                    O
                   //
              H-C
                 \
                  NH2
   - Several papers have been published describing the performance of
        AM1 vs. PM3:
Dewar, M. J. S.; Healy, E. F.; Yuan, Y.-C.; Holder, A. J. J. Comput. Chem.
        1990, 11, 541.
Smith, D.A. J. Fluor. Chem. 1990, 50, 427
Smith, D.A.; Ulmer, C.W.; Gilbert, M.J. J. Comput. Chem. 1992, 13, 640.
   - Most reserachers in my experience have stopped using PM3 and have
        returned to AM1.
                An Example of Parameterization Values for Aluminum
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          Parameter   AM1   MNDO   PM3
          Uss, eV   -24.353585   -23.807097   -24.845404
          Upp, eV   -18.363645   -17.519878   -22.264159
          zetas, au   1.516593   1.70288
                                        }   1.444161
          zetap, au   1.306347   1.073269
          betas, eV   -3.866822   -0.594301
                                        } -2.670284
          betap, eV   -2.317146   -0.956550
          alpha   1.976586   1.868839   1.521073

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        Gaussians:
        Intensity #1, eV     0.090000         -          -0.473090
        Width #1            12.392443         -           1.915825
        Position #1          2.050394         -           1.451728
        Intensity #2, eV         -           -          -0.154051
        Width #2                 -           -           6.005086
        Position #2              -           -           2.51997
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The point on the potential surface located by PM3 is significantly
different than that located by AM1. This is immediately apparent from the
large discrepancy between the Upp values. These are the important one-
electron energy values and they have strong influence on the parameter
hypersurface. Also, the difference between Uss and Upp for both MNDO and AM1
is about 6 eV. This has been reduced to 2.5 eV in PM3. The real difficulty,
however, is in the Beta values. These parameters are the two-center/one-
electron resonance terms and are responsible for bonding interactions between
atoms. The PM3 values are almost zero, resulting in the conclusion that
there is very little bonding between atoms involving aluminum! (Note that
the AM1 values for betas and betap spread out around the single MNDO value
for beta. This suggests that the MNDO values were reasonable and AM1 adds
greater flexibility.) PM3 regains the bonding interactions lost in the low
beta values with two strongly attractive Gaussians spanning the bonding region.

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