A Density Functional That Accounts for Medium-Range Correlation Energies in Organic Chemistry

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ABSTRACT

It has recently been pointed out that current density functionals are inaccurate for computing stereoelectronic effects and energy differences of isomerization reactions and isodesmic reactions involving alkanes; this has been interpreted as an incorrect prediction of medium-range correlation energies. This letter shows that the recently published M05-2X functional has good accuracy for all three of the recently highlighted problems and should be useful for a wide variety of problems in organic chemistry.

Density functional theory (DFT) is now the main tool for calculating the structure and energetics of complex molecular systems and materials.1 Recently, Grimme claimed that all state-of-the-art density functionals provide a qualitatively incorrect picture of the stereoelectronic effects in alkane isomers,2 and these observations are reinforced by two independent works3,4 in this journal. Table 1 compares Grimme’s results for four standard density functionals5–9 to experimentally derived2–10 data for the zero-point exclusive energy of n-octane minus that of 2,2,3,3-tetramethylbutane. All four density functionals that he studied get the sign wrong. Grimme2 pointed out that a related problem is the increasing size of the errors per bond in heats of formation and alkyl bond dissociation energies predicted by most density functionals when molecules get larger.3,11 We had

(10) NIST Standard Reference Database. See http://webbook.nist.gov/chemistry/
Table 1. Energy Difference (kcal/mol) between n-Octane and 2,2,3,3-Tetramethylbutane

<table>
<thead>
<tr>
<th>method</th>
<th>ΔE (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiment</td>
<td>+1.9</td>
</tr>
<tr>
<td>PBE</td>
<td>−5.5</td>
</tr>
<tr>
<td>TPSSH</td>
<td>−6.3</td>
</tr>
<tr>
<td>B3LYP</td>
<td>−8.4</td>
</tr>
<tr>
<td>BLYP</td>
<td>−9.9</td>
</tr>
<tr>
<td>B3PW91g</td>
<td>−7.0</td>
</tr>
<tr>
<td>M05-2X</td>
<td>+2.0</td>
</tr>
<tr>
<td>M05-2X</td>
<td>+1.4</td>
</tr>
<tr>
<td>MP2</td>
<td>+4.6</td>
</tr>
</tbody>
</table>

References: 2, 10. * Calculations were performed with the cQZV3P basis set and MP2/TZV(dp) geometries, and results were taken from ref 2. † Reference 6. ‡ References 7–9. § Reference 8. †† Present work with the 6-311+G(2df,2p) basis set; for all calculations in this table the geometry was optimized at the same level of theory and with the same basis set as was used for the calculation of the energy. † Reference 12. †‡ Present work with the cQZV3P basis set and MP2/TZV(dp) geometries. †§ Reference 15.

pointed out earlier that the new M05-2X density functional has much better performance than all previous density functionals for alkyl bond dissociation energies as a function of alkyl group size.12 Unfortunately, Grimme did not test the M05-2X density functional for this problem. In fact, we present work with the 6-311+G(2df,2p) basis set; the geometry was optimized at the same level of theory and with the same basis set as was used for the calculation of the energy. Reference 12. †‡ Present work with the aug-cc-pVTZ basis set. †§ Reference 15.

er et al.,4 who compared the energies of three isomers of (CH)12; see Figure 1. Table 3 compares their most accurate calculation and their DFT calculations to our M05-2X calculations. Again, the M05-2X functional does quite well.

We believe that the success of the M05-2X functional derives from the design of its functional form,12 building primarily on work of Becke,23,24 and from consistent, calculation and their DFT calculations to our M05-2X calculations. Again, the M05-2X functional does quite well.

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simultaneous parametrization\(^{12}\) of the M05-2X exchange and correlation functionals against a broad range of accurate data including noncovalent interactions for main group chemistry. This allowed us to better represent medium-range correlation energy. We note that the M05-2X functional involves kinetic energy density in both the exchange and correlation functionals, unlike fifth-rung functionals,\(^{25}\) it does not involve terms\(^{26}\) dependent on virtual orbitals.

The calculations were carried out with a modified version of Gaussian03.\(^{27}\) M05-2X is now available in release 5.0 of NWChem.\(^{28}\) In addition it is scheduled to be in the next minor revision of Gaussian03 and in the next release (version 7.0) of Jaguar.

The reader is referred to the original paper\(^{12}\) and references therein for further details of the M05-2X functional. In one of our previous papers,\(^{29}\) we analyzed the noncovalent interaction of methane with benzene and concluded that the success of M05-2X for this noncovalent interaction is due to its improved correlation functional for the description of medium-range correlation. We noted in ref 29 that although M05-2X does not give the asymptotic \(-\text{CoR}^6\) tail of the long-range interaction, it agrees with CCSD(T)/complete-basis results for CH\(_4\)-benzene within 0.17 kcal/mol from 3.4 to 5.4 Å (the minimum is 1.5 kcal/mol at 3.8 Å and is 4.6 times deeper than the value at 5.4 Å).

We also note that the M05-2X functional has been shown to outperform many other functionals for noncovalent interactions,\(^{12,29,30}\) for torsional potentials of conjugated polyenes,\(^{31}\) and for proton affinities of conjugated polyenes (a test of its ability to predict polarizabilities of conjugated double bonds).\(^{31}\) It is less satisfactory for energy differences\(^{32}\) between cumulenes and polyynes, but still better than all other functionals in Tables 1-3.\(^{31}\) M05-2X also has very high quantitative accuracy for main-group thermochemistry and barrier heights.\(^{12}\)

### Acknowledgment.

The authors are grateful to Stefan Grimme for sending us the MP2/TZVP/(d,p) geometries and cQZV3P basis set for octane isomers. This work was supported in part by the National Science Foundation by grant no. CHE03-49122 (quantum mechanics of complex systems) and by the Office of Naval Research under award no. N00014-05-1-0538 (software tools).

### Supporting Information Available:

Cartesian coordinates and electronic total energies of all molecules involved in this letter. This material is available free of charge via the Internet at http://pubs.acs.org.

| Table 3. Energies (kcal/mol) of (CH\(_2\))\(_n\) Isomers Relative to Structure 1 |
|-------------------------------|---|---|
| Method                        | 2 | 3 |
| CCSD(T)\(^{a}\)               | 14.3\(^{b}\) | 25.0\(^{a}\) |
| BLYP\(^{c}\)                  | -10.0\(^{b}\) | -11.5\(^{c}\) |
| G96LYP\(^{d}\)               | -6.4\(^{b}\) | -6.8\(^{d}\) |
| KMLYP\(^{e}\)                | 28.4\(^{b}\) | 41.7\(^{e}\) |
| B3LYP\(^{f}\)                | -0.2\(^{b}\) | 1.9\(^{f}\) |
| BHandHLYP\(^{g}\)            | 7.4\(^{b}\) | 14.0\(^{g}\) |
| B3PW91b\(^{h}\)              | 14.4\(^{b}\) | 19.8\(^{h}\) |
| M05-2X\(^{i}\)               | 14.0\(^{i}\) | 21.4\(^{i}\) |
| M05-2X\(^{j}\)               | 16.9\(^{j}\) | 25.4\(^{j}\) |
| MP2\(^{k}\)                  | 23.2\(^{k}\) | 31.2\(^{k}\) |

\(^{a}\) References 13, 19, and 20.\(^{b}\) From ref 4. For each functional and MP2, we give the result with the 6-311+G(d,p) basis set.\(^{c}\) Reference 7.\(^{d}\) Reference 21.\(^{e}\) Reference 22.\(^{f}\) Reference 7-9.\(^{g}\) Reference 23.\(^{h}\) Reference 8. Present work with the 6-311+G(2df,2p) basis set; the geometry was optimized at the same level of theory with the same basis set as was used for the calculation of the energy.\(^{i}\) Reference 12.\(^{j}\) Present work with the 6-311+G(d,p) basis set; the geometry was optimized at the same level of theory with the same basis set as was used for the calculation of the energy.\(^{k}\) Reference 15.


