Performance of DFT: The good, the bad, and the ugly

Structures and frequencies, electronic densities; Thermochemical properties: reaction energies and barriers;
Potential energy curves (for bond breaking);
Charged systems (H2+ example);
Weak interactions and dispersion;
Excited states (will discuss later).
**TABLE 3: Summary of the Benchmarking Studies on Density Functionals Published during the Last 4 Years, with Major Emphasis Being Given to Performance of B3LYP and Its Ranking among the Density Functionals Tested, and to the Best Functional for Each Property in Each Study**

<table>
<thead>
<tr>
<th>Study</th>
<th>Structure</th>
<th>av. value in the dataset</th>
<th>Basis set</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. bond lengths (Å)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.008</td>
<td>B3LYP (0.007)</td>
<td>17 first-row closed shell molecules</td>
<td>1.493</td>
<td>Aug-cc-PV5Z</td>
</tr>
<tr>
<td>0.006</td>
<td>MPW1K (0.01)</td>
<td>10 bond lengths</td>
<td>1.17</td>
<td>MG3S</td>
</tr>
<tr>
<td>0.008</td>
<td>B3LYP (0.008)</td>
<td>44 bond lengths</td>
<td>1.186</td>
<td>6-311+G**</td>
</tr>
<tr>
<td>0.014</td>
<td>MPW3LYP (0.013)</td>
<td>13 bond lengths</td>
<td>1.689</td>
<td>DZQ/TZQ</td>
</tr>
<tr>
<td>0.16</td>
<td>SVWN3 (0.05)</td>
<td>8 bond lengths</td>
<td>2.11</td>
<td>DZQ/TZQ</td>
</tr>
<tr>
<td>0.007</td>
<td>VSXC (0.006)</td>
<td>71 bond lengths</td>
<td>n/a</td>
<td>Aug-cc-pVQZ</td>
</tr>
<tr>
<td>0.73</td>
<td>B3LYP (0.75)</td>
<td>10 bond angles</td>
<td>108.99</td>
<td>MG3S</td>
</tr>
<tr>
<td>1.94</td>
<td>c-SVWNV (1.32)</td>
<td>16 bond lengths</td>
<td>1.186</td>
<td>6-311+G**</td>
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<tr>
<td>1.20</td>
<td>B3LYP (1.05)</td>
<td>34 bond angles</td>
<td>1.689</td>
<td>DZQ/TZQ</td>
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<tr>
<td>0.02</td>
<td>MPW3LYP (0.01)</td>
<td>4 distances</td>
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<td>MG3S</td>
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<tr>
<td>1.02</td>
<td>B97-1 (0.08)</td>
<td>6 barrier heights</td>
<td>11.85</td>
<td>MG3S</td>
</tr>
<tr>
<td><strong>B. angles (deg)</strong></td>
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<td></td>
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<td></td>
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<td>B3LYP (1.4)</td>
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<td>MG3S</td>
</tr>
<tr>
<td>4.31</td>
<td>BB1K (1.16)</td>
<td>42 barrier heights</td>
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<td>6-311+G**</td>
</tr>
<tr>
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<td>BB1K (1.50)</td>
<td>76 barrier heights</td>
<td>110.67</td>
<td>6-311+G**</td>
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<td>6-311+G**</td>
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<td>6-311+G**</td>
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<tr>
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<td>BB1K (1.05)</td>
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<td>Aug-cc-pVQZ</td>
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<tr>
<td>3.10</td>
<td>B97-1 (2.58)</td>
<td>6 barrier heights</td>
<td>12.29</td>
<td>Aug-cc-pVQZ</td>
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<td><strong>C. H bonds (Å)</strong></td>
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<td>0.02</td>
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<td>4 distances</td>
<td>2.81</td>
<td>MG3S</td>
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<tr>
<td>1.02</td>
<td>B97-1 (0.08)</td>
<td>6 barrier heights</td>
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<td>MG3S</td>
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<td><strong>D. weak interactions (Å)</strong></td>
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<tr>
<td>2.29</td>
<td>B3LYP (0.84)</td>
<td>88 compounds</td>
<td>253.84</td>
<td>MG3S</td>
</tr>
<tr>
<td>7.2</td>
<td>OLKY (3.1)</td>
<td>7 compounds</td>
<td>202.6</td>
<td>DZQ/TZQ</td>
</tr>
<tr>
<td>5.1</td>
<td>OLKY (4.25)</td>
<td>37 compounds</td>
<td>202.6</td>
<td>DZQ/TZQ</td>
</tr>
<tr>
<td>2.29</td>
<td>B98 (1.84)</td>
<td>13 compounds</td>
<td>38.16</td>
<td>MG3S</td>
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<tr>
<td>3.4</td>
<td>c-SVWNV (2.6)</td>
<td>58 compounds</td>
<td>32.55</td>
<td>6-311+G**</td>
</tr>
<tr>
<td>3.5</td>
<td>B98 (3.2)</td>
<td>25 compounds</td>
<td>32.55</td>
<td>6-311+G**</td>
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<td><strong>E. isomerizations</strong></td>
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<tr>
<td>2.29</td>
<td>mPWPW91 (9.5)</td>
<td>372 compounds</td>
<td>253.84</td>
<td>MG3S</td>
</tr>
<tr>
<td>17.8</td>
<td>BLYP (15.0)</td>
<td>223 compounds</td>
<td>253.84</td>
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<tr>
<td>7.0</td>
<td>B3PW91 (3.95)</td>
<td>156 compounds</td>
<td>253.84</td>
<td>MG3S</td>
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<tr>
<td>3.31</td>
<td>B98 (2.90)</td>
<td>148 compounds</td>
<td>253.84</td>
<td>MG3S</td>
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<tr>
<td>6.24</td>
<td>M05 (1.84)</td>
<td>3 pairs of compounds</td>
<td>8.17</td>
<td>6-311+G(2df,2p)</td>
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</table>

**Kinetics (kcal/mol)**

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<tr>
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<th>av. value in the dataset</th>
<th>Basis set</th>
<th>Ref.</th>
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<tr>
<td>2.19</td>
<td>B3LYP (2.19)</td>
<td>17 compounds</td>
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<tr>
<td>0.57</td>
<td>VSXC (0.5)</td>
<td>6 compounds</td>
<td>517.22</td>
<td>MG3S</td>
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<tr>
<td>0.90</td>
<td>X1B95 (0.52)</td>
<td>109 compounds</td>
<td>497.65</td>
<td>MG3S</td>
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<tr>
<td>0.61</td>
<td>MPW3LYP (0.43)</td>
<td>6 compounds</td>
<td>517.22</td>
<td>MG3S</td>
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<td>16.7</td>
<td>BLYP (5.3)</td>
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<td>DZQ/TZQ</td>
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<td>BLYP (5.8)</td>
<td>9 compounds</td>
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<td>DZQ/TZQ</td>
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<td><strong>B. binding energies</strong></td>
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<td>TPSS1KCS (5.4)</td>
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<td>M05 (7.8)</td>
<td>18 compounds</td>
<td>65.5</td>
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<td><strong>C. ionization potentials</strong></td>
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<td>253.84</td>
<td>MG3S</td>
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<td>3.8</td>
<td>B3LYP (3.8)</td>
<td>88 compounds</td>
<td>253.84</td>
<td>MG3S</td>
</tr>
<tr>
<td>7.2</td>
<td>OLYP (3.1)</td>
<td>7 compounds</td>
<td>202.6</td>
<td>DZQ/TZQ</td>
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<td>B1B95 (4.25)</td>
<td>37 compounds</td>
<td>202.6</td>
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<td>B98 (1.84)</td>
<td>13 compounds</td>
<td>38.16</td>
<td>MG3S</td>
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<td>3.4</td>
<td>c-SVWNV (2.6)</td>
<td>58 compounds</td>
<td>32.55</td>
<td>6-311+G**</td>
</tr>
<tr>
<td>3.5</td>
<td>B98 (3.2)</td>
<td>25 compounds</td>
<td>32.55</td>
<td>6-311+G**</td>
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<td>27.1</td>
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<td>253.84</td>
<td>MG3S</td>
</tr>
<tr>
<td>17.8</td>
<td>BLYP (15.0)</td>
<td>223 compounds</td>
<td>253.84</td>
<td>MG3S</td>
</tr>
<tr>
<td>7.0</td>
<td>B3PW91 (3.95)</td>
<td>156 compounds</td>
<td>253.84</td>
<td>MG3S</td>
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<tr>
<td>3.31</td>
<td>B98 (2.90)</td>
<td>148 compounds</td>
<td>253.84</td>
<td>MG3S</td>
</tr>
<tr>
<td>6.24</td>
<td>M05 (1.84)</td>
<td>3 pairs of compounds</td>
<td>8.17</td>
<td>6-311+G(2df,2p)</td>
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### TABLE 3 (Continued)

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<tr>
<th>Functional (MUE)</th>
<th>MUE</th>
<th>ranking</th>
<th>dataset size</th>
<th>dataset characteristics</th>
<th>av. value in the dataset</th>
<th>basis set</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nonbonded Interactions I</strong> (kcal/mol)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. H bonding</td>
<td>0.45</td>
<td>4/15</td>
<td>B97-1 (0.26)</td>
<td>4 binding energies</td>
<td>4 H-bonding dimers</td>
<td>9.38</td>
<td>MG3S</td>
</tr>
<tr>
<td></td>
<td>1.94</td>
<td>6/6</td>
<td>PWB6K (0.46)</td>
<td>5 binding energies</td>
<td>5 π H-bonding systems</td>
<td>4.49</td>
<td>MG3S</td>
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<tr>
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<td>0.77</td>
<td>21/44</td>
<td>B3P86 (0.46)</td>
<td>6 binding energies</td>
<td>6 H-bonding dimers</td>
<td>8.37</td>
<td>DZDZ/MP2/6-31G(d,p)/G2/MG3S</td>
</tr>
<tr>
<td></td>
<td>0.76</td>
<td>18/25</td>
<td>PBE1PBE (0.34)</td>
<td>6 binding energies</td>
<td>6 H-bonding dimers</td>
<td>8.37</td>
<td>MG3S</td>
</tr>
<tr>
<td></td>
<td>0.65</td>
<td>9/37</td>
<td>MPWLYP (0.31)</td>
<td>10 binding energies</td>
<td>10 H-bonding systems</td>
<td>7.15</td>
<td>Aug-cc-pVTZ</td>
</tr>
<tr>
<td>B. charge transfer</td>
<td>0.80</td>
<td>9/44</td>
<td>MPWB1K (0.50)</td>
<td>7 binding energies</td>
<td>7 charge-transfer complexes</td>
<td>4.63</td>
<td>DZDZ/MP2/6-31G(d,p)/G2/MG3S</td>
</tr>
<tr>
<td></td>
<td>0.63</td>
<td>9/25</td>
<td>PW6K (0.21)</td>
<td>7 binding energies</td>
<td>7 charge-transfer complexes</td>
<td>4.63</td>
<td>MG3S</td>
</tr>
<tr>
<td>C. dipole interactions</td>
<td>0.78</td>
<td>29/44</td>
<td>PBE1KCIS (0.36)</td>
<td>6 binding energies</td>
<td>6 dipole-interaction complexes</td>
<td>3.05</td>
<td>DZDZ/MP2/6-31G(d,p)/G2/MG3S</td>
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<tr>
<td></td>
<td>0.86</td>
<td>20/25</td>
<td>PW6K (0.28)</td>
<td>6 binding energies</td>
<td>6 dipole-interaction complexes</td>
<td>3.05</td>
<td>MG3S</td>
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<tr>
<td><strong>Nonbonded Interactions II</strong> (kcal/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>A. weak interactions</td>
<td>0.23</td>
<td>15/15</td>
<td>B97-1 (0.02)</td>
<td>4 binding energies</td>
<td>4 rare-gas dimers</td>
<td>0.08</td>
<td>MG3S</td>
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<tr>
<td></td>
<td>0.60</td>
<td>32/44</td>
<td>B97-1 (0.19)</td>
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<td>9 weak-interaction complexes</td>
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<td>DZDZ/MP2/6-31G(d,p)/G2/MG3S</td>
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<tr>
<td></td>
<td>0.35</td>
<td>21/25</td>
<td>B97-1 (0.10)</td>
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<td>7 weak-interaction complexes</td>
<td>0.22</td>
<td>MG3S</td>
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<tr>
<td></td>
<td>0.35</td>
<td>21/25</td>
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<td>10 binding energies</td>
<td>10 rare-gas dimers</td>
<td>0.16</td>
<td>Aug-cc-pVTZ</td>
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<tr>
<td>B. π−π interactions</td>
<td>8.52</td>
<td>6/6</td>
<td>PWB6K (1.86)</td>
<td>11 binding energies</td>
<td>6 nucleic acid bases complexes + 5 amino acid pairs</td>
<td>7.53</td>
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<tr>
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<td>24/25</td>
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<td>5 binding energies</td>
<td>5 π−π stacking complexes</td>
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<td>MG3S</td>
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</table>

*Average value of the property in the dataset used for evaluation. Nonbonded interactions in which electrostatic or orbital–orbital interactions are dominant and the dispersion contribution is small. Nonbonded interactions in which the dispersion contribution is dominant.*
Self-interaction error: \( \text{H}_2^+ \) example

Incorrect Dissociation Behavior of Radical Ions in Density Functional Calculations

Thomas Bally* and G. Narahari Sastry
TABLE XI. Dissociation energies of symmetric radical cations, $D_e = E(X) + E(X^+) - E(X^+_2, R_e)$ (in kcal/mol), where $R_e$ (in Å) is the equilibrium bond length. The reference values are taken from Ref. 71 for $H_2^+$, from Ref. 72 for $He_2^+$, from Ref. 73 for $Ne_2^+$, and from Ref. 74 for $Ar_2^+$.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ref.</th>
<th>$\omega$B97X</th>
<th>$\omega$B97</th>
<th>B97-1</th>
<th>B3LYP</th>
<th>BLYP</th>
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<tr>
<td>$H_2^+$</td>
<td>1.057</td>
<td>1.102</td>
<td>1.100</td>
<td>1.107</td>
<td>1.114</td>
<td>1.136</td>
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<tr>
<td>$He_2^+$</td>
<td>1.081</td>
<td>1.137</td>
<td>1.141</td>
<td>1.146</td>
<td>1.146</td>
<td>1.184</td>
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<tr>
<td>$Ne_2^+$</td>
<td>1.765</td>
<td>1.784</td>
<td>1.780</td>
<td>1.831</td>
<td>1.827</td>
<td>1.924</td>
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<tr>
<td>$Ar_2^+$</td>
<td>2.423</td>
<td>2.457</td>
<td>2.445</td>
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<td>2.536</td>
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<td>MSE</td>
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<td>0.035</td>
<td>0.069</td>
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<td>0.039</td>
<td>0.035</td>
<td>0.069</td>
<td>0.074</td>
<td>0.134</td>
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</tbody>
</table>

$D_e$ $R_e$ $H_2^+$ 64.4 68.4 68.5 68.9 67.9 69.1
$He_2^+$ 57.0 71.5 71.9 71.5 77.4 83.2
$Ne_2^+$ 32.2 54.0 56.0 58.5 59.4 73.1
$Ar_2^+$ 30.8 38.6 36.9 44.1 43.3 49.0
MSE 12.0 12.2 14.7 15.9 22.5
MAE 12.0 12.2 14.7 15.9 22.5

FIG. 1. Dissociation curve of $Ar_2^+$ curve. Zero level is set to $E(Ar) + E(Ar^+)$ for each method.
Figure 3: Independent comparison of an established GGA (BLYP) against an established hybrid (B3LYP), a recent range-separated hybrid (\(\omega\)B97X), and a range-separated hybrid that includes an empirical long-range dispersion correction (\(\omega\)B97X-D). MAE (mean average errors) are computed for the atomization energies (48 reactions comprising the G3/05 test set) and weak interactions (25 intermolecular complex binding energies).\(^{23,24}\)