Short Course on
Density Functional Theory and Applications
VI. Applications

Samuel B. Trickey
©Sept. 2008
Quantum Theory Project
Dept. of Physics and Dept. of Chemistry
trickey@qtp.ufl.edu
**Evaluation of Functionals: GGA better than MP2**

- Comparison of structural and energetic properties for 32 small molecules calculated with various DFT and conventional methods using a 6-31G(d) basis set. [B.G. Johnson, P.M.W. Gill, J.A. Pople, J. Chem. Phys. 98, 5612 (1993)]

**Average deviation (AD) & average absolute deviation (AAD) from experiment**

<table>
<thead>
<tr>
<th>Method</th>
<th>Bond distances (pm)</th>
<th>Bond angles (degree)</th>
<th>Harmon. vibrational frequencies (cm$^{-1}$)</th>
<th>Atomization energies (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AD</td>
<td>AAD</td>
<td>AD</td>
<td>AAD</td>
</tr>
<tr>
<td>SVWN</td>
<td>1.4</td>
<td>2.1</td>
<td>-0.7</td>
<td>1.9</td>
</tr>
<tr>
<td>BVWN</td>
<td>1.8</td>
<td>1.8</td>
<td>-0.8</td>
<td>2.0</td>
</tr>
<tr>
<td>BLYP</td>
<td>2.0</td>
<td>2.0</td>
<td>-1.6</td>
<td>2.3</td>
</tr>
<tr>
<td>HF</td>
<td>-1.0</td>
<td>2.0</td>
<td>0.1</td>
<td>2.0</td>
</tr>
<tr>
<td>MP2</td>
<td>1.0</td>
<td>1.4</td>
<td>-0.9</td>
<td>1.8</td>
</tr>
<tr>
<td>QCISD</td>
<td>1.2</td>
<td>1.3</td>
<td>-0.9</td>
<td>1.8</td>
</tr>
</tbody>
</table>

- LDA (SVWN) reproduces geometries and vibrational frequencies with very satisfactory accuracy, but binding energies are much too large
- Gradient corrections (either to the exchange only, B-VWN, or at the GGA level, BLYP) do not yield more accurate structural data and vibrational frequencies, but significantly improve binding energies
- GGA yields substantially better energies than conventional methods like MP2 and QCISD
**Evaluation of Functionals: Hybrid XC Functional Energetics**

- Comparison of average absolute deviations (AAD) of *formation enthalpies* (kJ mol\(^{-1}\)) calculated from various XC functionals (LDA, GGA, B3 hybrid parameterized models) relative to experiment, for the five subsets of molecular types which comprise the G2 neutral test set (non-hydrogen molecules, hydrocarbons, substituted hydrocarbons, radicals, and inorganic hydrides); 6-311+G(3df,2p) basis set  [L.A. Curtiss, K. Ragavachari, P.C. Redfern, and J.A. Pople J. Chem. Phys. 106, 1063 (1997)]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SVWN</td>
<td>308</td>
<td>559</td>
<td>520</td>
<td>228</td>
<td>141</td>
</tr>
<tr>
<td>BP86</td>
<td>69</td>
<td>108</td>
<td>112</td>
<td>66</td>
<td>34</td>
</tr>
<tr>
<td>BPW91</td>
<td>51</td>
<td>20</td>
<td>33</td>
<td>27</td>
<td>18</td>
</tr>
<tr>
<td>BLYP</td>
<td>43</td>
<td>34</td>
<td>26</td>
<td>25</td>
<td>13</td>
</tr>
<tr>
<td>B3PW91</td>
<td>22</td>
<td>17</td>
<td>12</td>
<td>13</td>
<td>8</td>
</tr>
<tr>
<td>B3LYP</td>
<td>22</td>
<td>12</td>
<td>9</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>G2</td>
<td>11</td>
<td>5</td>
<td>8</td>
<td>6</td>
<td>4</td>
</tr>
</tbody>
</table>

- GGA: here BLYP and BPW91 GGA better than BP86
- Hybrid B3 functionals are quite accurate, but note that the parameters were fitted to this kind of molecules
- G2 scheme errors only half as large as those of the best XC (B3LYP)
**Evaluation of Functionals: Reaction Barriers**

- Comparison of average absolute (AAD) and maximum deviations (MaxD) of barrier heights (kJ mol\(^{-1}\)) for 12 small-molecule organic reactions for two conventional methods, HF and MP2, and the BLYP and B3PW91 density functionals. [J. Baker, M. Muir, and J. Andzelm, J. Chem. Phys. 102, 2063 (1995)]

<table>
<thead>
<tr>
<th></th>
<th>AAD</th>
<th>MaxD</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>57</td>
<td>128</td>
</tr>
<tr>
<td>MP2</td>
<td>41</td>
<td>120</td>
</tr>
<tr>
<td>BLYP</td>
<td>25</td>
<td>92</td>
</tr>
<tr>
<td>B3PW91</td>
<td>15</td>
<td>54</td>
</tr>
</tbody>
</table>

- Barrier heights present a serious problem for all these methods
- LDA (not shown) is particularly unreliable:
  - LDA yields a stable minimum for \( \text{H}_3 \) instead of the saddle point of the reaction \( \text{H}_2 + \text{H} \rightarrow \text{H} + \text{H}_2 \)
  - This spectacular failure caused by insufficient self-interaction correction
- GGA (BLYP) is comparable to MP2, but B3PW91 is noticeably better, although not of chemical accuracy
- Barriers calculated with approx. XC functionals tend to be somewhat too low.

Credit: N. Rösch
**Evaluation of Functionals: Organometallic Molecule Energetics**

Dissociation energies (kJ mol\(^{-1}\)) of the first transition metal (TM) carbonyl bond \(\text{M(CO)}_n \rightarrow \text{M(CO)}_{n-1} + \text{CO}\) for various DFT and conventional methods compared with experiment

<table>
<thead>
<tr>
<th></th>
<th>Ni(CO)(_4)</th>
<th>Fe(CO)(_5)</th>
<th>Cr(CO)(_6)</th>
<th>Mo(CO)(_6)</th>
<th>W(CO)(_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA (^{(a)})</td>
<td>188</td>
<td>276</td>
<td>260</td>
<td>220</td>
<td>202</td>
</tr>
<tr>
<td>BP86 (^{(a)})</td>
<td>120</td>
<td>187</td>
<td>192</td>
<td>160</td>
<td>162</td>
</tr>
<tr>
<td>BP86+rel.corr. (^{(a)})</td>
<td>125</td>
<td>191</td>
<td>193</td>
<td>166</td>
<td>183</td>
</tr>
<tr>
<td>MP2 (^{(b)})</td>
<td>187</td>
<td>–</td>
<td>243</td>
<td>193</td>
<td>230</td>
</tr>
<tr>
<td>Cl-MCPF (^{(c)})</td>
<td>100</td>
<td>163±21</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CCSD(T) (^{(d)})</td>
<td>125</td>
<td>–</td>
<td>192</td>
<td>169</td>
<td>201</td>
</tr>
<tr>
<td>Exp. (^{(e)})</td>
<td>105±8</td>
<td>176</td>
<td>154±8</td>
<td>169±8</td>
<td>192±8</td>
</tr>
</tbody>
</table>

- LDA shows substantial overbinding, GGA yields significant improvement
- Only very expensive many-body methods (CCSD(T), MCPF) are comparable to GGA accuracy
- \(\text{Cr(CO)}_6\) is a difficult system for all methods compared here
- Relativistic effects are small for first-row TM atoms, noticeable for second-row TMs, and large for third-row TMs
- References on next slide

Credit: N. Rösch
Evaluated of Functionals: Organometallic Molecule Energetics

References

<table>
<thead>
<tr>
<th></th>
<th>Ni(CO)₄</th>
<th>Fe(CO)₅</th>
<th>Cr(CO)₆</th>
<th>Mo(CO)₆</th>
<th>W(CO)₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA (a)</td>
<td>188</td>
<td>276</td>
<td>260</td>
<td>220</td>
<td>202</td>
</tr>
<tr>
<td>BP86 (a)</td>
<td>120</td>
<td>187</td>
<td>192</td>
<td>160</td>
<td>162</td>
</tr>
<tr>
<td>BP86+rel.corr. (a)</td>
<td>125</td>
<td>191</td>
<td>193</td>
<td>166</td>
<td>183</td>
</tr>
<tr>
<td>MP2 (b)</td>
<td>187</td>
<td>–</td>
<td>243</td>
<td>193</td>
<td>230</td>
</tr>
<tr>
<td>CI-MCPF (c)</td>
<td>100</td>
<td>163±21</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CCSD(T) (d)</td>
<td>125</td>
<td>–</td>
<td>192</td>
<td>169</td>
<td>201</td>
</tr>
<tr>
<td>Exp. (e)</td>
<td>105±8</td>
<td>176</td>
<td>154±8</td>
<td>169±8</td>
<td>192±8</td>
</tr>
</tbody>
</table>


Credit: N. Rösch
**DFT Studies – Spin-orbit Splitting in Graphene**


Graphene

\[ \varepsilon(k) = \hbar c a \kappa \]

\[ c_g = \frac{\partial \varepsilon}{\partial k} \]

A-B Graphite

Massless Dirac Fermions

\[ \varepsilon_{\text{Fermi}} \]

← Toward M  Toward Γ →

FIG. 1. Bare Kohn-Sham energy bands (eV) and density of states (states/eV atom) for the graphite 1L. Both are referred to \( E_F \) as zero of energy. Solid (dashed) curve: even (odd), i.e., \( \varepsilon(k) \) symmetry with respect to reflection in the system plane.
DFT Studies – Spin-orbit Splitting in Graphene

Spin-orbit gap (recent published values)

Kane & Mele [Phys. Rev. Lett 95, 226801 (2005)]: $\Delta_{SO} \approx 0.1 \text{ meV} \approx 1.2 \text{ K}$
{pert. theory estimate; part of prediction of Quantum Spin Hall Effect}

Huertas-Hernando, Guinea, and Brataas [Phys. Rev. B 74, 155426 (2006)]: $\Delta_{SO} \approx 0.0009 \text{ meV} \approx 0.01 \text{ K}$
{tight-binding estimate}

Min et al. [Phys. Rev. B 74, 165310 (2006)]: $\Delta_{SO} \approx 0.0011 \text{ meV} \approx 0.013 \text{ K}$
{tight-binding + PAW pseudo-potential checks}

Yao et al. [Phys. Rev. B 75, 041401 (2007)]: $\Delta_{SO} \approx 0.0008 \text{ meV} \approx 0.009 \text{ K}$
{tight-binding + plane-wave, separable relativistic pseudo-potential checks}
**DFT Studies – Spin-orbit Splitting in Graphene**


<table>
<thead>
<tr>
<th>Lattice parameter (a.u.)</th>
<th>HL-LDA (meV)</th>
<th>PBE LDA (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.621</td>
<td>0.0504</td>
<td>0.0505</td>
</tr>
<tr>
<td>4.85205</td>
<td>0.0408</td>
<td>0.0408</td>
</tr>
<tr>
<td>4.38995</td>
<td>0.0646</td>
<td>0.0648</td>
</tr>
</tbody>
</table>

Our calculations – All electron, large GTO basis, tight tolerances:

\[ \Delta_{SO} \approx 0.05 \text{ meV} \approx 0.6 \text{ K} \]

Relatively insensitive to lattice constant. Roughly same size as estimated by Kane and Mele. Tight-binding and pseudo-potential values are way too small.
Graphene Rolled into Single-wall Carbon Nanotube

FIG. 1: Two-dimensional graphene lattice structure. Primitive lattice vectors $R_1$ and $R_2$ are depicted in origin unit cell. Rollup vector $R$ is shown for (7,3) SWNT. Armchair nanotubes are defined by rollup vectors along the $(n, n)$ direction, zigzag nanotubes are defined by rollup vectors along the $(n, 0)$ direction. Armchair and zigzag nanotubes will possess reflection planes and be achiral, all other SWNTs will be chiral.

Credit: R.K. Vadapalli
and J.W. Mintmire
Structure of Multi-walled Chiral CNTs

LSDA structural results

<table>
<thead>
<tr>
<th>CNT</th>
<th>(7,3)</th>
<th>(12,8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>diameter (nm)</td>
<td>0.70</td>
<td>1.38</td>
</tr>
<tr>
<td>h (nm)</td>
<td>0.0486</td>
<td>0.0496</td>
</tr>
<tr>
<td>φ (degrees)</td>
<td>214.2</td>
<td>215.5</td>
</tr>
<tr>
<td>unit cell atoms</td>
<td>4</td>
<td>8</td>
</tr>
</tbody>
</table>

Intershell distance 0.34 nm

Interface energy

- $0.10 \text{ eV/atom}$
- $1.2 \text{ J/m}^2$

Energetics comparable to earlier work on achiral armchair nanotubes by Charlier & Michenaud, PRL (1993).

Credit: J.W. Mintmire
Band Structure of $C(12,8)/C(7,3)$ Double-walled CNT

(a) $C(7,3)$ band structure
(b) $C(12,8)$ band structure
(c) $C(7,3)/C(12,8)$ composite band structure

12 atoms in unit cell

Credit: J.W. Mintmire
Density of KS States for C(12,8)/C(7,3) Double-walled CNT

Credit: J.W. Mintmire
Energetics of Coaxial SWNTs

Preliminary results indicate energetic preference for 3-4 Å separations.
Equilibrium Conformations and Electronic Structures of Metallic CNWs

(5,5) CNW with Chain at X=1.5 Å

(8,8) CNW

(7,7) CNW with Chain at X=1.5 Å

X = radial offset of chain from center

Credit: J.W. Mintmire
DFT Studies – (111) Li Ultra-thin Films

Are there work function Quantum Size Effects (QSE) with number of layers in a real UTF? (vs. Schulte’s Jellium model)[J.C. Boettger and SBT, Phys. Rev. B 45, 1363-72 (1992)]

Work function QSE is modest; steps in DOS are not.
**DFT Studies – (111) Al Ultra-thin Films**

Surface energy variation with number of layers $\mathcal{N}$.

Are the oscillations spurious? Bottom curve: independently calculated solid cohesive energy subtraction. Top curve: incrementally calculated solid energy.


\[
E_{\text{surf}}(\mathcal{N}) = \lim_{\mathcal{N} \to \infty} \frac{1}{2} \left[ E_{\mathcal{N}}^{\text{bind,cell}} - \mathcal{N} E_{\text{solid}}^{\text{bind,cell}} \right]
\]

\[
\approx \frac{1}{2} \left[ E_{\mathcal{N}}^{\text{bind,cell}} - \mathcal{N} E_{\text{incremental}}^{\text{bind,cell}} (\mathcal{N}_{\text{max}}) \right]
\]

\[
E_{\text{incremental}}^{\text{bind,cell}} (\mathcal{N}) = E_{\mathcal{N}}^{\text{bind,cell}} - E_{\mathcal{N}-1}^{\text{bind,cell}}
\]

Instead, fit data as function of $\mathcal{N}$ to

\[
E_{\mathcal{N}}^{\text{bind,cell}} = \mathcal{N} E_{\text{solid}}^{\text{bind,cell}} + 2E_{\text{surf}}(\mathcal{N})
\]

and extract surf formation energy from intercept (average over QSE)
**DFT Studies – (111) Al Ultra-thin Films**

Work function variation with number of layers $\mathcal{N}$.

![Graph showing work function variation](image)

**FIG. 1.** Calculated work functions vs the number of layers for the LCGTO-FF calculations using 37 (solid line) and 19 BZ points (dashed line).
DFT Studies – (111) δ-Pu Ultra-thin Films

Surface energy (Left) and Work Function (Right) variation with number of layers. 
NSP = Non-Spin Polarized; SR = Scalar Relativistic; SO = Spin-Orbit corrected

DFT Studies – Spin Cusps in Transition Metal Monolayers


![Graphs showing spin-magnetic moments and work functions](image)

**Interpretation (hex):** cusp sequence with decreasing $r_{ws}$ is from bands crossing $\varepsilon_F$ with symmetries $M_2, \Gamma_6$, and $K_1$.

**Hex:** $E_{coh} = -4.95$ eV/atom, $r_e = 2.32$ au, $\mu_e = 2.45$

**Sq:** $E_{coh} = -4.57$ eV/atom, $r_e = 2.35$ au, $\mu_e = 2.29$
DFT Studies – Spin Cusps in Transition Metal Monolayers

FIG. 3. Electronic band structure of a ferromagnetic hexagonal Fe monolayer with a lattice constant of 5.85 a.u.; (a) majority spin bands and (b) minority spin bands. Solid (dashed) lines denote states with even (odd) symmetry under reflection through the plane of the nuclei. Due to space limitations, a number of the symmetry labels have been neglected (see Fig. 1). Also, for the M and K points, the labels for the even (odd) states are on the left (right).

FIG. 4. Electronic band structure and DOS for a ferromagnetic hexagonal Fe monolayer with $a = 4.40$ a.u.; (a) majority-spin bands and (b) minority-spin bands. The same notation is used as in Fig. 3.
DFT Studies – Spin Cusps in Transition Metal Monolayers

• Here are Cr hex and square 1Ls [SBT (unpublished, 1997-98) for Ti, V, Cr]

Hex: 1 cusp in $\mu$ and in $\epsilon_F$

Square: 3 cusps in $\mu$, 2 seen in $\epsilon_F$

Ground state, $E_{coh}=-3.235$ eV/atom, $A_e = 16.587$ au$^2$, $\mu=0$

Ground state, $E_{coh}=-3.235$ eV/atom, $A_e = 16.651$ au$^2$, $\mu_e =0$
DFT Studies – *ab initio* Molecular Dynamics

**MD** is incredibly successful in Materials Physics. It is just Newton’s 2nd Principle \[ m_i \ddot{R}_i = -\nabla_i V(R_1, R_2, \ldots, R_N) \]

In principle, the potential for nuclear motion is the **Born-Oppenheimer energy surface**

\[ V(\{R\}) = E_0(\{R\}) + E_{\text{nucl}}(\{R\}) \]

where \( E_0(\{R\}) \) is the ground state *electronic* energy. If this is done (instead of using an empirical potential), the procedure is called “*ab initio MD*” or B-O MD.

---

**FIG. 1.** Relaxed structure of \((\text{H}_2\text{O})_n\)-silica chain at time=0. panel (a) depicts a water dimer \((n=2)\) with the chain and (b) a monolayer water film with the chain \((n=160)\).

**FIG. 3.** (Color) Upper panel gives counts of various defects in the \((\text{H}_2\text{O})_{160}\)-\(\text{SiO}_2\) chain as a function of time; the lower ones depict the struc-