Density-fitted periodic local MP2. Application to molecular crystals and surface adsorption

Denis Usvyat

Institut für Physikalische und Theoretische Chemie, Universität Regensburg
Universitätsstraße 31, D-93040 Regensburg

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CRYSCOR overview I

Provides a periodic local MP2 solutions on top of the HF reference, provided by the CRYSTAL code.

CRYSCOR takes (from CRYSTAL):

- The information on the **basis set, geometry, symmetry, etc**
- **Density and Fock matrices** of the **periodic HF** solution
- Symmetrized **Wannier functions**

CRYSCOR delivers:

- **periodic LMP2 energy**
- **periodic LMP2 density matrices** (presently without an orbital relaxation)

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The DFP-LMP2 (density fitted periodic local MP2) method comprises:

- Molecular local correlation techniques: PAOs for virtuals, excitation domains, orbital pairs
- Extensive use of symmetry
- Two-step multipole-constrained Density Fitting approximation
- Distant-pair two-electron integrals – via multipole expansion
- The contribution from the very distant pairs – through evaluation of $C_6$ parameters
The CRYSCOR crew

<table>
<thead>
<tr>
<th>Torino</th>
<th>Regensburg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prof. Cesare Pisani</td>
<td>Prof. Martin Schütz</td>
</tr>
<tr>
<td>Dr. Lorenzo Maschio</td>
<td>Dr. Denis Usvyat</td>
</tr>
<tr>
<td>Dr. Silvia Casassa</td>
<td></td>
</tr>
<tr>
<td>Migen Halo</td>
<td></td>
</tr>
</tbody>
</table>

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LMP2 and weakly bound systems

- **Unlike DFT** LMP2 is able to treat dispersion, which plays an important role in such systems!

- **Wannier functions are well localized** within the monomers $\Rightarrow$ the periodic LMP2 calculations are relatively not expensive.

- **However**, for describing the weak binding **large basis sets are needed**.
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DFT and dispersion, argon dimer

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## CO$_2$ crystal

<table>
<thead>
<tr>
<th>Method</th>
<th>Formation energy kcal mol$^{-1}$</th>
<th>Lattice constant Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF, 6-21G*</td>
<td>2.59</td>
<td>6.09</td>
</tr>
<tr>
<td>HF, 6-311G(3D)</td>
<td>1.95</td>
<td>6.13</td>
</tr>
<tr>
<td>LDA, 6-21G*</td>
<td>7.46</td>
<td>5.26</td>
</tr>
<tr>
<td>LDA, 6-311G(3D)</td>
<td>8.48</td>
<td>5.28</td>
</tr>
<tr>
<td>B3LYP, 6-21G*</td>
<td>1.89</td>
<td>6.01</td>
</tr>
<tr>
<td>B3LYP, 6-311G(3D)</td>
<td>1.40</td>
<td>6.01</td>
</tr>
<tr>
<td>LMP2, 6-21G*</td>
<td>4.51</td>
<td>5.79</td>
</tr>
<tr>
<td>LMP2, 6-21G* $\rightarrow$ AVQZ</td>
<td>5.95</td>
<td>5.65</td>
</tr>
<tr>
<td>LMP2, 6-311G(3D)</td>
<td>5.76</td>
<td>5.68</td>
</tr>
<tr>
<td>LMP2, 6-311G(3D) $\rightarrow$ AVQZ</td>
<td>6.50</td>
<td>5.63</td>
</tr>
<tr>
<td>Experiment</td>
<td>6.44</td>
<td>5.54</td>
</tr>
</tbody>
</table>

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Physisorption on a surface.

Pair Partitioning

- Adsorbate-adsorbate pairs
- Adsorbate-slab pairs
- Within-slab pairs

New approximation: Only important pairs can be included in the calculations. For example, only slab-adsorbate pairs can be taken into account.
What we lose:

intra  disp.  disp-exch  ionic  BSSE

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The electrostatic interaction remains at the HF level.
What we gain:

- If electrostatic interaction doesn’t dominate, the approximation is fairly good. For adsorption of methane on MgO its error is $\approx 0.5$ kJ/mol.

- This error can be reduced further by including just few adsorbate-adsorbate and within-slab pairs.

- The calculations become essentially less consuming without a large loss in accuracy.

- No LMP2 BSSE by construction.

- Possibility to treat molecular adsorption on metallic surfaces.
Methane on MgO

Dipod

Tripod

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<table>
<thead>
<tr>
<th>Method</th>
<th>Preferable structure</th>
<th>Adsorption energy, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semiempirical</td>
<td>Tripod</td>
<td></td>
</tr>
<tr>
<td>PCI-extrapolated MCPF Methane on MgO cluster*</td>
<td>Dipod</td>
<td>8</td>
</tr>
<tr>
<td>DFT**</td>
<td>Dipod</td>
<td></td>
</tr>
<tr>
<td>*<em>DFP-LMP2, 8-511G</em>(MgO)/6-311G(3d)(CH₄)</td>
<td>Dipod</td>
<td><strong>10.1</strong></td>
</tr>
<tr>
<td>Experiment</td>
<td>Dipod</td>
<td><strong>13.1</strong></td>
</tr>
</tbody>
</table>


Physisorption on a metallic surface

- HF is bad for metals
- MP2 is totally inappropriate for metals

But

- We are not interested in the metal but rather in the adsorption on it.
- DFT for dispersion is worse than HF for a metal.
- Adsorbatelayer does not conduct

Therefore

We can try to model the dispersion by MP2 by considering only the slab-adsorbate (and if needed adsorbate-adsorbate pairs)

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H₂ physisorbed on graphene.

(A common work with together with Thomas Heine and Lyuben Zhechkov in the context of hydrogen storage)

R.H. Lochan and M. Head-Gordon, PCCP, 8, 2006

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H$_2$ on graphene

Graphene is a metal (semimetal)...

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Band structure of graphene

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But the states of the adsorbed $H_2$ molecules form narrow bands with a band gap!
Band structure of $\text{H}_2$ on graphene

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DOS of $H_2$ on graphene

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So the **LMP2 method can be applied** for **H$_2$** physisorbed on graphene **if within-slab pairs are not included.**
H$_2$ on graphene

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### Adsorption energies for H\textsubscript{2} on graphene and related structures

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>Adsorption energy, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>MP2/6-31G</em></td>
<td>H\textsubscript{2} on benzene</td>
<td>1</td>
</tr>
<tr>
<td><em>MP2/6-311G</em>*</td>
<td>H\textsubscript{2} on benzene</td>
<td>2.1</td>
</tr>
<tr>
<td>*MP2/aug-cc-pVQZ</td>
<td>H\textsubscript{2} on benzene</td>
<td>5</td>
</tr>
<tr>
<td>*MP2/aug-cc-pVQZ</td>
<td>H\textsubscript{2} on coronene</td>
<td>6.4</td>
</tr>
<tr>
<td>Experiment</td>
<td>H\textsubscript{2} on graphene</td>
<td>5</td>
</tr>
<tr>
<td>LMP2/6-31G*(C)/6-311G**(H)</td>
<td>H\textsubscript{2} on graphene</td>
<td>2.4</td>
</tr>
</tbody>
</table>

*T. Heine, L. Zhechkov, G. Seifert, PCCP 6 (2004)*

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Timings for DFP-LMP2 calculations

<table>
<thead>
<tr>
<th>System and basis set</th>
<th>CPU time for HF, sec</th>
<th>CPU time for DFP-LMP2, sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ crystal, 6-21G*</td>
<td>30</td>
<td>3500</td>
</tr>
<tr>
<td>CO₂ crystal, 6-311G(3d)</td>
<td>300</td>
<td>17000</td>
</tr>
<tr>
<td>CH₄ on MgO, 6-311G(3d)/8-511G*</td>
<td>4500</td>
<td>9500</td>
</tr>
<tr>
<td>H₂ on graphene, 6-311G**/6-31G*</td>
<td>700</td>
<td>5000</td>
</tr>
</tbody>
</table>

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Conclusions and outlook

The DFP-LMP2 method, implemented in CRYSCOR code is evidently a convenient and reliable tool in studying weakly bound periodic systems.

**Problems:**

- A need for larger basis sets $\Rightarrow$ dual basis sets, F12-technique (work in progress).

- Poorly localized Wannier functions in conducting slabs $\Rightarrow$ Utilization of finite-support Wannier functions.
Localization of Wannier function

A Wannier function for diamond

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Localization of Wannier function

A Wannier function for diamond

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Localization of Wannier function

A Wannier function for diamond

D. Usvyat and M. Schütz, TCA (2005)

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Acknowledgments

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My collaborators:

- Regensburg theory group:
  Prof. Martin Schüetz
  Keyarash Sadeghian
  Danylo Kats
  Dominik Schemmel

- Cryscor Group in Torino:
  Prof. Cesare Pisani
  Dr. Lorenzo Maschio
  Dr. Silvia Casassa Migen Halo

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