Some Correlation Problems – and One Partial Solution

A partially solved problem
  He scattering from MgO(100)

An interesting problem
  Polyacetylene (again)

The ultimate problem (unsolved, obviously)
  Magnetocaloric cooling of systems like (Ca,La)MnO$_3$
1. He Scattering From MgO(100)
A Well Defined Problem (for an oxide surface)
The Experiment

1. Elastic Diffraction
2. Inelastic energy loss
3. Resonance in traps
4. Trapping
The Problem – Compute the Potential

Weak interaction – London dispersion at long range
Methodology

CRYSTAL14 – local Gaussian orbitals

Truncated summation of analytic integrals on the periodic lattice => exact exchange calculated efficiently

Hybrid exchange: B3LYP functional (20% Fock exchange) (Reliablity established now in some 100+ periodic systems)

Triple / Quadruple + polarisation valence basis sets

http://www.crystal.unito.it
Who did the hard work – CRYSTAL / CRYSCOR

A reliable and efficient code for periodic MP2 theory
Local functions describing the occupied manifold

Local functions describing the virtual manifold

Truncation of the occupied space: Wannier-Wannier pairs

Reduction of the virtual space: PAOs & W-W pair domains
Scaling with system size

Single processor AMD Opteron 2.2 GHz
MgO(100)-He

2x2 supercell (negligible lateral interactions)
5 layer slab + extrapolation to infinite slab
HF + LMP2 Binding

$D \sim 4 \text{ meV}$

Measured 7.5-12 meV
FIG. 4: Comparison of the CC intensities for case 1 (red stars) and case 2 (blue circles) with the experimental spectra (black lines) and the peak areas (black squares). Diffraction peaks are given in counts/s; peak areas and CC intensities have been normalized in a way that the specular (central) peak appears at the maximum of the experimental peak. The considered incident energy are the following: (a) $E_i = 26.62$ meV, (b) $E_i = 33.30$ meV, (c) $E_i = 40.02$ meV, (d) $E_i = 48.96$ meV, (e) $E_i = 50.20$ meV and (f) $E_i = 60.47$ meV.
Pragmatic Approaches….. (Fiddling)

Scaling the MP2 contribution by comparison to CCSD(T) in model systems:

\[ E = \text{HF} + 1.65 \times \text{MP2} \]

Close the single particle gap and the MP2 contribution increases suggesting:

\[ E = \text{B3LYP} + \text{MP2(B3LYP)} \]

Both give similar energy surfaces with a deeper minimum…
Computed Binding Energy: He-MgO(100)

Well depth measured: 7.0 - 12.5 meV
MP2 [4 meV]
MP2(B3LYP) [6.7 meV]
Comparison with Measured He Scattering

Incident Energies (meV)

a. 26.62
b. 33.30
c. 40.02
d. 48.96
e. 50.20
f. 60.47
### Bound States

<table>
<thead>
<tr>
<th></th>
<th>Exp.1 (meV)</th>
<th>Exp.2 (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$</td>
<td>---</td>
<td>-10.2</td>
</tr>
<tr>
<td>$E_1$</td>
<td>-5.5</td>
<td>-5.3</td>
</tr>
<tr>
<td>$E_2$</td>
<td>-2.6</td>
<td>-2.4</td>
</tr>
<tr>
<td>$E_3$</td>
<td>-1.2</td>
<td>-0.9</td>
</tr>
<tr>
<td>$E_4$</td>
<td>-0.5</td>
<td>-0.6</td>
</tr>
<tr>
<td>$E_5$</td>
<td>-0.3</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

Approaching the Exact Energy Surface

Calculate the difference between the MP2 energy and the exact energy using a finite cluster

\[ \sum_z \left( \Delta E^{CCSD(T)} - \Delta E^{LMP2} \right) \]

Systematically improve:

1. Theory: MP2 – CCSD – CCSD(T) – CCSDT(Q)
2. Basis Set: aug-cc-VDZ – VTZ – VQZ
3. Cluster size:
For $\text{Na}_2\text{Mg}_3\text{O}_4$ Cluster  Scaled MP2 Energy
Approaching the Exact Answer (Lateral Average)

A deeper bound state in the potential… but error analysis suggests that 10.2eV is not present

Reasonable agreement with the diffraction intensities
A deeper bound state in the potential... but error analysis suggests that 10.2eV is not present

Reasonable agreement with the diffraction intensities
A powerful method for surface analysis if the potential is known.

It seems that it is possible to get close to the exact potential in a systematic way but only with some effort.
High quality data for LiF (etc), TiO$_2$ ....

Solving for a structure requires a simple potential model.

1. Develop a pairwise O$^{2-}$-He interaction potential (none of the obvious functional forms fit well) and test transferability

2. A much faster method with $\sim$1meV accuracy
2. Polyacetylene
Peierls Distortion

B3LYP nospin - equal CC distances

B3LYP nospin dimerised
# Energy Gap and Bond Length Alternation

<table>
<thead>
<tr>
<th>Method</th>
<th>$a$ (Å)</th>
<th>C-C (Å)</th>
<th>BLA (Å)</th>
<th>$\chi_C$</th>
<th>$E_g$ (eV)</th>
<th>$\Delta E$ (eV)</th>
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</thead>
<tbody>
<tr>
<td>EXP</td>
<td>2.46</td>
<td>1.36, 1.44</td>
<td>0.08</td>
<td>-</td>
<td>1.4-1.9</td>
<td>-</td>
</tr>
<tr>
<td>B3LYP</td>
<td>2.467</td>
<td>1.363, 1.424</td>
<td>0.061</td>
<td>0.514</td>
<td>1.246</td>
<td>0.015</td>
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<tr>
<td>LDA</td>
<td>2.450</td>
<td>1.379, 1.391</td>
<td>0.012</td>
<td>0.503</td>
<td>0.102</td>
<td>0.000</td>
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<tr>
<td>HF</td>
<td>2.460</td>
<td>1.328, 1.455</td>
<td>0.126</td>
<td>0.529</td>
<td>7.270</td>
<td>0.146</td>
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</tbody>
</table>
Spin Polarisation – Symmetric Geometry

<table>
<thead>
<tr>
<th>spin moment $^{(\mu_B)}$</th>
<th>B3LYP</th>
<th>LDA</th>
<th>HF</th>
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</thead>
<tbody>
<tr>
<td>$</td>
<td>S</td>
<td>_C$</td>
<td>0.22</td>
</tr>
<tr>
<td>$</td>
<td>S</td>
<td>_H$</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Spin Polarisation vs Dimerisation

B3LYP spin - equal CC distances

B3LYP nospin dimerised

Same energy (~0.3 meV) in B3LYP
Band gap after spin or spatial (or both) symmetry breaking always ~1eV
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