Quantum Chemical Investigations of Phenol and Larger Aromatic Molecules on TiO₂ Surface

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LITH-IFM-EX--04/1317--SE
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Adsoption of organic molecules at a surface of titanium dioxide (101) anatase is studied using quantum-chemical density functional theory. Anatase can be used in solar cells. For the clean anatase surface the band gap is so large that only UV-light can excite electrons. Different groups with conjugated systems are attached to obtain a more suitable band gap.

Phenol was attached in different positions to a cluster of anatase and geometry optimized using the B3LYP-functional. The geometry that was energetically most favorable was used to put in phenylmethanol, phenylethanol, naphthol, 2-phenanthrol, 1-pyrol and 2-perylol.

To give a more realistic model of phenol at anatase, a study of a two-dimensional periodic anatase surface was also made. Molecular orbitals were calculated to study the overlap between HOMO and LUMO orbitals. The calculation shows that phenol will remain as a molecule and will not dissociate.

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The band gap gets smaller when molecules are attached at the cluster and with 2-perylol it reaches the energy of visible light.

The molecular orbitals for HOMO, LUMO and LUMO of the adsorbed molecule were investigated. HOMO was localized at the molecule, LUMO at the cluster and LUMO of the adsorbed molecule move closer to the energy of LUMO when the number of rings increases.
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1. **Abstract**

Adsorption of organic molecules at a surface of titanium dioxide (101) anatase is studied using quantum-chemical density functional theory. Anatase can be used in solar cells. For the clean anatase surface the band gap is so large that only UV-light can excite electrons. Different groups with conjugated systems are attached to obtain a more suitable band gap.

Phenol was attached in different positions to a cluster of anatase and geometry optimized using the B3LYP-functional.

The geometry that was energetically most favorable was used to put in phenylmethanol, phenylethanol, naphthol, 2-phenanthrol, 1-pyrol and 2-perylol. To give a more realistic model of phenol at anatase, a study of a two-dimensional periodic anatase surface was also made.

Molecular orbitals were calculated to study the overlap between HOMO and LUMO orbitals.

The calculation shows that phenol will remain as a molecule and will not dissociate.

The band gap gets smaller when molecules are attached at the cluster and with 2-perylol it reaches the energy of visible light.

The molecular orbitals for HOMO, LUMO and LUMO of the adsorbed molecule were investigated. HOMO was localized at the molecule, LUMO at the cluster and LUMO of the adsorbed molecule move closer to the energy of LUMO when the number of rings increases.
2. Introduction

The development of better solar cells is an important and interesting field. The solar cell consists of a surface with transition metal oxide (Grätzel M 1989). In a solar cell the energy of light is absorbed and an electron is excited from the valence band to the conducting band in the transition metal oxide. It could for example be titanium dioxide, TiO$_2$.

This compounds have a relatively big band gap, which means that they only can adsorb ultra violet, high energy, light of approximately 220 nm wavelength, to excite an electron.

Many experimental and theoretically efforts are made in this area, with attaching different molecules at the transition metal oxide surface. Examples of molecules attached are formic acid (Persson et al. 2002b and Vittadini et al. 2000) and isonicotinic acid (Persson et al. 2002a).

If a large molecule with a conjugated system is attached at the surface, light with lower energy than UV-light, in the visible range, also can be adsorbed. If a conjugated system with ruthenium is put on the surface, the band gap gets smaller and the system can absorb light with a lower energy, up to yellow light with a wavelength of about 580 nm. (Hagfeldt & Grätzel 2000)

![Diagram of energy levels for anatase and a molecule](image)

**Figure 1:** The band gap between HOMO and LUMO for anatase and the molecule is at different energy level. An electron can also be excited from the molecule to the cluster.
Here a surface of titanium dioxide (101) anatase was studied. Different groups with conjugated systems were attached to minimize the band gap. At first phenol was attached in different positions to a cluster of titanium dioxide, anatase (101) and geometry optimized with B3LYP. The case that was energetically most favorable was used to put in phenylmethanol, phenylethanol, naphthol, 2-phenanthrol, 1-pyrol and 2-perylool. All calculations were preformed in gas phase. To give a more realistic model of phenol at anatase, there was also a small study computing on periodic anatase. Molecular orbitals were also calculated to see the possible overlap between HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), (figure 1). The band gap of the different combinations of molecules at the surface where compared to see if a larger conjugated system can catch light with lower energy.
3. Method

3.1. Computations

The geometries were optimized using B3LYP computations. The B3LYP computing method stems from ab initio theory and density function theory, (DFT). A special basis set is used (see appendix). The used basis set is collected from two different articles (Lunell et al. (1997) and Persson & Ojamäe (2000)). The computing for the cluster was done with the computer program Gaussian03/98 and the computing for the periodic surface was done with the computer program Crystal03.

The calculations were preformed in gas phase. In an attempt to verify the accuracy of the used basis set for the calculations, the formation energy for phenol, from carbon dioxide and water, was computed. The geometry of the cluster was optimized before other molecules were attached and all the adsorbates were optimized before they were attached to the surface.

3.2. The anatase cluster

Because the long computations time for large systems, the study was done on a small part of the anatase surface, in stead of the entire surface. A cluster of TiO$_2$, anatase (101), was cut out from the surface. The used cluster of TiO$_2$ consists of 8 Ti, 14 O and 4 OH (Figure 2). The OH-groups is added in the corner to neutralize the cluster. In a large surface all titanium will be five or six coordinated. In the anatase cluster Ti1 and Ti3 are five coordinated and Ti2 and Ti4 are just four coordinated.

3.3. Phenol

The biggest effort is made with phenol at the anatase surface. Calculations of the adsorption energy of phenol on an anatase cluster were made. The phenol was put on the surface of the cluster, with the OH-group towards the cluster, in different positions to get the best possible adsorption energy. Dissociativ adsorption where a proton is transferred from the phenol oxygen to a surface oxygen was also studied.
3.4. **Periodic surface**
To get a more realistic view of the state, a computing on a periodic surface was done. The slab was twice as thick as in the cluster model.

3.5. **Spacer groups**
Spacer groups were put into the molecule. They are intending to make a distance between the conjugated system and the surface, to see what effects it makes in adsorption energy and band gap. In phenylmethanol there is one CH$_2$-group put in between the ring of phenol and OH-group and in phenylethanol there are two CH$_2$-groups put in (figure 3). Then they were put in at the best position of phenol at the cluster surface and optimized in the same way as phenol.

![Figure 3: Phenylmethanol and phenylethanol.](image)
3.6. **Larger molecules**

To get a larger conjugated system more rings were added on to the phenol in the energetically most favorable position. Molecules with up to five benzene rings were constructed and optimized.

There were 1-naphthol and 2-naphthol (Figure 4) put in the same position and then geometry optimized in the same way as phenol.

![Figure 4: 1-naphthol and 2-naphthol](image)

For even larger molecules there were phenanthrene, pyrene and perylene with one hydrogen of each substituted against a hydroxyl group, see figure 5 for structure. They were also put in the best position for phenols but the energies for them were just single point computed.

![Figure 5: The 2-phenanthrol, 1-pyro and 2-perylol that were attached at the anatase and single point computed.](image)
3.7. **Molecular orbital and band gap**
Molecular orbitals were computed to see where the orbitals were located. Most interesting are the HOMO and LUMO. The lowest unoccupied molecular orbital that is located on the adsorbed molecule (LUMO-ads) is also of interest. LUMO-ads are an important orbital because an electron can be excited within the molecule and then be transported to the cluster. The energy levels of the molecular orbitals gives the band gap that shows the energy that is needed to excite an electron from HOMO to LUMO or to a higher unoccupied energy level. Band gaps and molecular orbital were compared for anatase and the different sizes of attached molecules at the surface.

3.8. **Rotation of the benzene ring in phenol**
An attempt with rotating the benzene ring in phenol was made (figure 13). The phenols OH-group was fixed at the cluster surface and the benzene ring was rotated around the CO-axis. The rotation was made in steps of five degrees, from 0 to 180 degrees. Molecular orbitals and band gap variations during the rotation were studied.
4. Results

4.1. Phenol adsorption geometry at the surface

Different possible adsorption geometries for phenol at the surface are given from the optimizations. The different adsorption geometries and energies are given in Table 1. When there are several numbers for titanium, the adsorbate oxygen forms a bidentate bond to the titanium ions. In the case with unprotolyzed phenol the hydrogen has hydrogen bonds to the surface, in the protolyzed case it is covalent bond. In figure 6 the atoms in the cluster were marked to see to which atom at the surface the atoms from phenol attach. Figure 7 shows the different geometries. Then the energies where compared to get the best adsorption energy.

![Figure 6: An illustration of the used anatase cluster with the important atoms marked.](image)

Table 1: Adsorption geometry of phenol at the anatase cluster. The table shows to which atom in the anatase cluster, the oxygen and hydrogen of the phenol where bonded. When there are several numbers for titanium, the oxygen is between them. For the number see fig 6. Unprotolyzed or protolyzed is for the phenol if it is complete or if the hydrogen is put somewhere else. The adsorption energy is the difference between the energy of the free cluster and molecule minus the energy of the complex. Under mode the geometries are named and they are shown in figure 7.

<table>
<thead>
<tr>
<th>O at Ti number</th>
<th>H at O number</th>
<th>Unprotolyzed or protolyzed</th>
<th>Adsorption energy kJ/mol</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2</td>
<td>7</td>
<td>Unprotolyzed</td>
<td>92</td>
<td>a</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>Unprotolyzed</td>
<td>82</td>
<td>b</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>Unprotolyzed</td>
<td>78</td>
<td>c</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>Unprotolyzed</td>
<td>66</td>
<td>d</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>Unprotolyzed</td>
<td>50</td>
<td>e</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>Unprotolyzed</td>
<td>40</td>
<td>f</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>Protolyzed</td>
<td>63</td>
<td>g</td>
</tr>
<tr>
<td>3, 2, 1</td>
<td>9</td>
<td>Protolyzed</td>
<td>43</td>
<td>h</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>Protolyzed</td>
<td>39</td>
<td>i</td>
</tr>
<tr>
<td>HO- at 2, 3</td>
<td>Ring at 8</td>
<td>Protolyzed</td>
<td>36</td>
<td>j</td>
</tr>
<tr>
<td>1, 2</td>
<td>8</td>
<td>Protolyzed</td>
<td>26</td>
<td>k</td>
</tr>
</tbody>
</table>
Figure 7: The different geometries for phenol attached at the surface. Phenol is unprotolyzed in a-f and protolyzed in g-k. The index a-k is from table 1.
4.2. **Adsorption energies**

The adsorption energies for the different attached molecules were compared. The best adsorption energy of phenol, the adsorption energies for the molecules with spacer groups and for the larger molecules are given in table 2.

Table 2: Adsorption energy of the different complexes. The adsorption energy is the difference between the energy of the free cluster and molecule minus the energy of the complex.

<table>
<thead>
<tr>
<th>Attached molecule</th>
<th>Adsorption energy kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol</td>
<td>92</td>
</tr>
<tr>
<td>phenylmethanol</td>
<td>118</td>
</tr>
<tr>
<td>phenylethanol</td>
<td>116</td>
</tr>
<tr>
<td>1-naphthol</td>
<td>67</td>
</tr>
<tr>
<td>2-naphthol</td>
<td>91</td>
</tr>
<tr>
<td>phenanthrol</td>
<td>87</td>
</tr>
<tr>
<td>pyrol</td>
<td>89</td>
</tr>
<tr>
<td>perylol</td>
<td>91</td>
</tr>
</tbody>
</table>

4.3. **Periodic surface**

For the periodic surface the two adsorption geometries with best energies were computed. A comparison of the adsorption energies between the cluster and the periodic surface gave the result in table 3, with a and b from table 1.

A comparison of the atoms coordinates between the cluster and the periodic surface shows that the distances for the different model do not change much if a molecule was attached. But when the coordinates in the cluster was compared with the coordinates in the cluster with attached phenol the maximum difference was within 0.2 Å. The same comparison with the periodic surface gave a maximum difference of 0.09 Å.

Table 3: Adsorption energy for phenol attached at the cluster and at the periodic surface.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Adsorption energy at the cluster kJ/mol</th>
<th>Adsorption energy at the periodic surface kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>92</td>
<td>96</td>
</tr>
<tr>
<td>b</td>
<td>82</td>
<td>91</td>
</tr>
</tbody>
</table>
4.4. Molecular orbital

Molecular orbitals for phenol, naphthol and perylol at anatase are shown in figure 8-10. The total HOMO is localized at the molecule and the total LUMO is localized at the anatase cluster. For phenol the LUMO-ads are localized 32 orbitals above the total LUMO but for the perylol the LUMO-ads are localized only 3 orbitals above the total LUMO.

Figure 8 HOMO, LUMO and LUMO in the molecule for phenol at anatase.

Figure 9 HOMO, LUMO and LUMO in the molecule for naphthol at anatase.

Figure 10 HOMO, LUMO and LUMO in the molecule for 5ring at anatase.
4.5. **Band gap**

The electronic Density Of States, DOS, which represent the band gap, for anatase and anatase with attached molecules are shown in figure 11. In the case with anatase the band gap goes from HOMO at $-7.5$ eV to LUMO at $-2.5$ eV. Compare with the case of phenol at anatase where the band gap goes from $-6.0$ eV to $-2.5$ eV. In the phenol case HOMO gets higher due to the phenol at the surface. The dotted line at about 0 eV is the LUMO-ads. The case with perylol adsorbed at the cluster gives an even smaller band gap from $-5$ eV to $-2.5$ eV. There was also an interesting change in the LUMO at the molecule, which has moved much closer to the band gap.
Figure 11: DOS for the anatase surface, phenol at surface, naphthol at surface, phenanthrol at surface, pyrol at surface and perylol at surface. A comparison of the band gaps with different groups attached. The dotted line represent the lowest unoccupied molecular orbital located at the molecule.
Figure 12: DOS for the anatase surface, phenol at surface, phenylmethanol at surface and phenylethanol at surface. A comparison of the band gaps with different spacer groups attached. The dotted line represent the lowest unoccupied molecular orbital located at the molecule.

The variation in DOS for a spacer group molecule at the surface compared with anatase and phenol at anatase is shown in figure 12.
The needed energy to cross the band gap can be expressed in the wavelength of light. A comparison of the wavelengths for different molecules is made in Table 4. The LUMO of the adsorbate shows that the wavelengths are approximately the same for the free and attached molecule. For the molecule of phenol the wavelength that can be adsorbed was 206 nm and when it was attached at the surface the wavelength was 200 nm within the molecule. The complex with phenol at the surface adsorbed a wavelength of 301 nm.

Table 4: The band gap for just the molecules, the anatase cluster and the molecules at the surface and the band gap within the molecule that is adsorbed at the cluster. The band gap is between HOMO and LUMO in the first case and between HOMO and LUMO of the adsorbate in the second case.

<table>
<thead>
<tr>
<th></th>
<th>LUMO E (eV)</th>
<th>LUMO wavelength (nm)</th>
<th>LUMO in adsorbate E (eV)</th>
<th>LUMO in adsorbate wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>6,02</td>
<td>206</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenylmethanol</td>
<td>6,50</td>
<td>191</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenylethanol</td>
<td>6,59</td>
<td>188</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-naphthol</td>
<td>4,61</td>
<td>269</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-naphthol</td>
<td>4,68</td>
<td>265</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-phenanthrol</td>
<td>4,65</td>
<td>267</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-pyrol</td>
<td>3,85</td>
<td>322</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-perylol</td>
<td>3,06</td>
<td>406</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anatase</td>
<td>5,59</td>
<td>222</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol+anatase</td>
<td>4,12</td>
<td>301</td>
<td>6,21</td>
<td>200</td>
</tr>
<tr>
<td>Phenylmethanol+anatase</td>
<td>4,69</td>
<td>265</td>
<td>6,42</td>
<td>193</td>
</tr>
<tr>
<td>Phenylethanol+anatase</td>
<td>4,47</td>
<td>278</td>
<td>6,53</td>
<td>190</td>
</tr>
<tr>
<td>Naphthal+anatase</td>
<td>3,23</td>
<td>384</td>
<td>4,47</td>
<td>277</td>
</tr>
<tr>
<td>2-phenanthrol+anatase</td>
<td>3,56</td>
<td>348</td>
<td>4,75</td>
<td>261</td>
</tr>
<tr>
<td>1-pyrol+anatase</td>
<td>3,16</td>
<td>393</td>
<td>3,85</td>
<td>322</td>
</tr>
<tr>
<td>2-perylol+anatase</td>
<td>2,83</td>
<td>439</td>
<td>3,02</td>
<td>410</td>
</tr>
</tbody>
</table>
4.6. **Rotation of the benzene ring in phenol**

During the rotation of the ring the band gap vary between 4.1 to 4.5 eV (figure 13), which correspond to a difference in wavelength of 301 to 274 nm. Figure 13 can be compared with the DOS-curve (figure 11) with HOMO to the left of the band gap and LUMO to the right of it. In the DOS-curve the orbital energy are widened, but in the rotating it is easier to see the change with exact bands for the energies. HOMO that is localized at the adsorbate changes a little, LUMO that is localized at the surface is fixed.

![Figure 13: The band gap changing during the rotation. (eV)](image)
How the adsorption energy varies during the rotation is shown in figure 14. When the rotation start, at 0 degree, the molecule is in its optimized position and has the lowest energy. At approximately 75 degree the curve reach a local maximum, at 90 degree it reaches a local minimum and at 115 degree it reaches the total maximum for the energy. At 180 degree the energy is down at the start energy level and the ring is in the same position as the start.

Figure 14: How the adsorption energy changes with the rotation of the ring.
The molecular orbitals of HOMO, LUMO and LUMO-ads for the rotating benzene ring are shown in figure 15. The distribution of HOMO and LUMO appears to be the same during the rotation of the ring, but for LUMO-ads the distribution changes.

Rotated 0 degrees

Rotated 45 degrees

Rotated 90 degrees

Rotated 135 degrees

Figure 15: Molecular orbital of phenol on anatase, for HOMO, LUMO and LUMO-ads, when the ring is rotated 45 degrees in each step.
4.7. **Formation energy**

For the verification of the basis sets accuracy, the formation energy for phenol was computed. The energy of phenol, carbon dioxide and water were calculated with B3LYP in the Gaussian program with the current basis set. The formation of phenol was taken from this reaction formula:

\[
6 \text{CO}_2 + 3 \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{OH} + 7 \text{O}_2
\]

Formula for computing the formation energy:

\[
E = (\text{C}_6\text{H}_5\text{OH}) + 7 (\text{O}_2) - (6 (\text{CO}_2) + 3 (\text{H}_2\text{O}))
\]

The result is compared with experimental values from SI Chemical Data (Aylward & Findlay 1998).

\[
\Delta H_{\text{Gaussian}} = 3437 \text{ kJ/mol} \quad \Delta H_{\text{SI}} = 2994 \text{ kJ/mol}
\]

\[
\Delta G_{\text{Gaussian}} = 3475 \text{ kJ/mol} \quad \Delta G_{\text{SI}} = 3036 \text{ kJ/mol}
\]

The agreement was within ten percent, which seems to be relatively good. In this verification formation energy are computed, with strong covalent bonds to build and break. For the rest of this work the adsorption energy are computed, with weaker intermolecular bonds. In this comparison the accuracy seems to be good.
5. Discussion

5.1. Phenol

Depending on that all titaniums in the cluster are under coordinated, it is better for the phenol to attach at Ti1 and Ti3 instead of Ti2 and Ti4 (see figure 6 for the numbers). Phenol seems to prefer to attach to Ti1 rather than to Ti3. When the hydrogen is separated from phenol, the molecule attaches to both Ti1 and Ti3 with the hydrogen attached to some oxygen at the surface.

For the energetically most favorable position of phenol (Figure 16), the hydrogen in the hydroxyl group is a little bit twisted out from the benzene ring plane.

For the protonized phenol at the surface the energy is 2/3 of the energy for the unprotonized. This means that the molecule prefers to be in the unprotonized form.

5.2. Other molecules attached

A spacer group seems to decrease the steric repulsion therefore they are getting a better adsorption energy. But they have a larger band gap compared with phenol at the surface.

In the case with 1-naphthol the molecule are lying more on the surface which increase the repulsion and the adsorption energy gets lower. For the other larger molecules with two to five rings, the adsorption energies are relatively constant.

5.3. Periodic surface

The movements of the atoms position are smaller for the periodic model than for the cluster when a molecule was attached. The distances between the titanium 1, 2, 3 and 4 (see figure 6 for numbers) changes less than 0.01 Å relative each other in the periodic model, for the same atoms in the cluster they move up to 0.07 Å relative each other.

For O5 that is between the titaniums the movements are small to, less than 0.03 Å for both models. O6 that is only two coordinated and sticks up from the surface have a larger movement. It moves up to 0.09 Å for the periodic model and up to 0.14 Å for the cluster. Largest difference is for the O10, which is placed in the middle of the surface in the periodic model respective at the bottom of the cluster. This gives a large movement in the cluster of up to 0.19 Å and a much smaller movement in the periodic surface with only up to 0.08 Å.
5.4. **Molecular orbitals and band gap**

The molecular orbitals of the anatase cluster with attached molecules follow the orbitals of the separate molecules. The HOMO was localized at the adsorbed molecule and the LUMO was localized at the anatase cluster. The LUMO-ads was following the energy trend from the LUMO of the isolated molecule. The trend seen from this was that the band gap was getting smaller when larger conjugated molecules were attached. When a perylol was attached the absorption reach up to visible light.

5.5. **Rotation of the benzene ring in phenol**

The attempt with rotating the benzene ring in phenol shows how it is possible to manipulate the band gap for the complex with small changes of the ring position.

The molecular orbitals for HOMO and LUMO seem to be almost the same during the rotation. For LUMO-ads the orbital change during the rotation. When the ring is rotated 90 and 135 degrees a large part of the orbital is localized at the cluster, which gives a better overlap for the excitation.
6. **Conclusions**
All the best energies comes from geometries where the oxygen of the phenol are attached to Ti1 and because of that it is five coordinated it seems to be a good approximation for a periodic model. A spacer group gives a better adsorption energy but a larger band gap compared with phenol at the surface. The adsorption energy for larger molecules with two to five rings seems to be relatively constant, with only smaller changes. The HOMO was localized at the attached molecule and the LUMO was localized at the cluster. The energy level for LUMO-ads was following the energy of the LUMO of the adsorbed molecule. The band gap was getting smaller when larger conjugated molecules were attached, with perylol the absorption reaches up to visible light. The attempt with rotating the benzene ring in phenol shows how it is possible to manipulate the band gap for the complex with small changes of the ring position. The most interesting molecular orbital was the LUMO-ads that change during the rotation.

7. **Acknowledgment**
I would like to thank my supervisor Lars Ojamäe for his grateful leading and support. I would also like to thank my friend Annika Lenz for all help and discussions.
8. References


9. Appendix

Basis sets and ECP

Ti 0
SP  1  1.00
  0.484000  1.000000  1.000000
D  4  1.00
  25.143600  0.023466
  6.797600  0.134297
  2.162500  0.350609
  0.749900  0.480195
D  1  1.00
  0.224800  1.000000
****

O 0
SP  3  1.00
  19.591534  0.00720200  0.05421843
  4.432019 -0.39948154  0.30323754
  1.129740  1.24851576  0.77624788
SP  1  1.00
  0.281139  1.000000  1.000000
****

C 0
SP  3  1.00
  11.502220  0.00491500  0.02892100
  2.459758 -0.17638900  0.17976400
  0.597261  0.54394300  0.52566200
SP  1  1.00
  0.155986  1.000000  1.000000
****

H 0
S  3  1.00
  0.1873113696D+02  0.3349460434D-01
  0.6401216923D+00  0.8137573262D+00
S  1  1.00
  0.1612777588D+00  0.1000000000D+01
****
Ti 0
BARTHE 3 18
local term
0
1 = 0 projection
1
2  1.0188263  12.272461
1 = 1 projection
1
2  0.7040588   7.745528
l = 2 projection
4
0  1.5920749 -0.559903
1  1.5920749 -7.742157
2  1.5920749   6.704284
4  1.5920749 -6.208391
O 0
BARTHE 2 2
local term
0
1 = 0 projection
2
1  10.373870   1.647681
2  10.373870  45.078280
l = 1 projection
1
2  25.320090  -7.790734
C 0
BARTHE 2 2
local term
0
1 = 0 projection
2
1  5.330459   1.369255
2  5.330459  21.035110
l = 1 projection
1
2  14.061160  -6.052015