Supplementary material

Electric field gradients in Hg compounds: Molecular orbital (MO) analysis and comparison of 4-component and 2-component (ZORA) methods

Vaida Arcisauskaite\textsuperscript{1*}, Stefan Knecht\textsuperscript{2}, Stephan P. A. Sauer\textsuperscript{1} and Lars Hemmingsen\textsuperscript{1}

1. Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

2. Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark

*Corresponding author. E-mail: vaida@chem.ku.dk
Herein, we compare the performance of Hartree-Fock (HF), BH&H and BP86 functionals at the 4-component level in calculating electron configuration of Hg, charges $q$ of Hg and Cl, polarisation terms (gross populations) (Table 1) and MO contributions to $V_{zz}$ at Hg (Table 2) in HgCl$_2$. On the one hand, the net charges of Hg and Cl are increasing along the series BP86 $\rightarrow$ BH&H $\rightarrow$ HF. On the other hand, the population of Hg 6p orbitals is decreasing along the series. This causes increasing negative contributions to $V_{zz}$ from the Hg core (mainly Hg 5p) and Hg6p + Cl MOs and total $V_{zz}$ values due to growing polarisation, including a partial cancellation due to decreasing electron donation from occupied Cl orbitals to the formally empty Hg 6p orbitals.

Table S1: Electron configuration of Hg, charge $q$ of Hg and Cl and polarisation terms (gross populations) in HgCl$_2$ obtained by projection analysis at the 4-component level using HF, BH&H and BP86 functionals.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>BH&amp;H</th>
<th>BP86</th>
</tr>
</thead>
<tbody>
<tr>
<td>5d</td>
<td>9.858</td>
<td>9.850</td>
<td>9.839</td>
</tr>
<tr>
<td>6s</td>
<td>0.805</td>
<td>0.941</td>
<td>1.066</td>
</tr>
<tr>
<td>6p</td>
<td>0.142</td>
<td>0.250</td>
<td>0.342</td>
</tr>
<tr>
<td>$q$ Hg</td>
<td>1.194</td>
<td>0.960</td>
<td>0.752</td>
</tr>
<tr>
<td>$q$ Cl</td>
<td>-0.530$\times$2</td>
<td>-0.429$\times$2</td>
<td>-0.328$\times$2</td>
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<tr>
<td>polar term</td>
<td>0.134</td>
<td>0.102</td>
<td>0.096</td>
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</table>

Table S2: MO contributions to $V_{zz}$ at Hg in HgCl$_2$ obtained at the 4-component level using Hartree-Fock (HF), BH&H and BP86 functionals and the UKB condition.

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>BH&amp;H</th>
<th>BP86</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sum$ Hg core:</td>
<td>-3.14</td>
<td>-0.11</td>
<td>2.11</td>
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<tr>
<td>$\sum$ Cl core:</td>
<td>-0.36</td>
<td>-0.36</td>
<td>-0.36</td>
</tr>
<tr>
<td>$\sum$ Hg5d + Cl MOs:</td>
<td>2.44</td>
<td>2.64</td>
<td>2.63</td>
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<tr>
<td>$\sum$ Hg6p + Cl MOs:</td>
<td>-11.85</td>
<td>-11.77</td>
<td>-10.46</td>
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<tr>
<td>Total $V_{zz}$:</td>
<td>-12.91</td>
<td>-9.60</td>
<td>-6.08</td>
</tr>
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</table>
Figure S1: Bond length $r$(Hg-Cl) dependence of Hg-Cl binding energy calculated with different Hamiltonians at the DFT/BH&H level.

Figure S2: Angle $\angle$(Cl-Hg-Cl) dependence of Hg-Cl binding energy calculated with different Hamiltonians at the DFT/BH&H level.
<table>
<thead>
<tr>
<th>MO Nr.</th>
<th>E [e.u.]</th>
<th>MONr.</th>
<th>E [e.u.]</th>
<th>MO Nr.</th>
<th>E [e.u.]</th>
<th>MO Nr.</th>
<th>E [e.u.]</th>
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<tbody>
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<td>45</td>
<td>-0.9412</td>
<td>45</td>
<td>-0.9267</td>
<td>55</td>
<td>0.004</td>
<td>Cl 3s 1/2; 1/2</td>
<td>0.0288</td>
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<tr>
<td>46</td>
<td>-0.9190</td>
<td>46</td>
<td>-0.9185</td>
<td>46</td>
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<td>Cl 3p 1/2; 1/2</td>
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<td>47</td>
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<td>0.9185</td>
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<td>49</td>
<td>0.3876</td>
<td>49</td>
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<td>Cl 3s 1/2; 1/2</td>
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<td>0.3876</td>
<td>50</td>
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<td>0.3876</td>
<td>51</td>
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<td>Cl 3s 1/2; 1/2</td>
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<tr>
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<td>-0.4500</td>
<td>52</td>
<td>0.3876</td>
<td>52</td>
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<td>0.3876</td>
<td>53</td>
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<td>54</td>
<td>0.3876</td>
<td>54</td>
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<td>0.3876</td>
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<td>0.008</td>
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Figure S3: AO contributions to MOs obtained for the linear and bent HgCl\textsubscript{2} with projection analysis at the 4-component level using the BH&H functional and the RKB condition.
Figure S4: Energies and a graphical representation of valence MOs in linear and bent HgCl$_2$, HgI$_2$ (isosurface: 0.015) and their contributions to V$_{zz}$ obtained at the SR-ZORA-4 level using the BH&H functional; red colour corresponds to the MOs with an admixture of Hg 6p and their contributions to V$_{zz}$.