Note on the Calculation of Analytical Hessians in the Zeroth-Order Regular Approximation (ZORA)

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ABSTRACT: The previously proposed atomic zeroth-order regular approximation (ZORA) approach, which was shown to eliminate the gauge dependent effect on gradients and to be remarkably accurate for geometry optimizations, is tested for the calculation of analytical second derivatives. It is shown that the resulting analytic second derivatives are indeed exact within this approximation. The method proves to yield frequencies that are remarkably close to the experimental frequency for uranium hexafluoride but less satisfactory for the gold dimer. © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 106: 2525–2528, 2006

Key words: ZORA; analytical Hessian; scalar relativistic

Introduction

For highly accurate quantum chemical calculations, the effects of relativity can hardly be ignored. Relativistic effects may be crucial to explain the reaction dynamics when heavy elements, of special interest in catalysis, are involved, even at the Hartree–Fock or density functional theory (DFT) level. The zeroth-order relativistic approximation (ZORA) [1, 2] was rediscovered during the 1990s [3–5] and has recently again experienced a surge of interest [6, 7]. This approach in its simplest scalar form reduces the Dirac equation [8] to a one-component equation in which the kinetic energy operator is replaced by a potential dependent operator:

$$\frac{p^2}{2m} \Rightarrow p \cdot \frac{1}{2c^2 - V} \cdot p. \quad (1)$$

Matrix elements of the kinetic energy operator thus become [9]:
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\[ (T^{ZORA})_{\mu \nu} = \left\langle \phi_{\mu} \right| p \cdot \frac{1}{2c^2 - V} \cdot p \left| \phi_{\nu} \right\rangle, \]  

(2)

where \( V \) is the Coulomb potential due to electrons and nuclei. Within the context of DFT theory, the inverse operator is generally determined using numerical integration. In our approach we used a resolution of the identity operator employing a suitably chosen orthogonalized internal basis and a matrix inversion [10]. To recover the correct relativistic limit, the kinetic energy operator is split of

\[ (T^{ZORA})_{\mu \nu} = -\frac{1}{2} \left\langle \phi_{\mu} \right| p^2 \left| \phi_{\nu} \right\rangle - \frac{1}{2} \sum_{\lambda} \left\langle \phi_{\mu} \right| \hat{p} \left| \phi_{\lambda} \right\rangle \left\langle \phi_{\lambda} \right| \hat{p} \left| \phi_{\nu} \right\rangle 
\]

\[ + \frac{1}{2} \sum_{n,k} \left\langle \phi_{\mu} \right| \hat{p} \left| \phi_{n,k} \right\rangle \left\langle \phi_{n,k} \right| \frac{2c^2 - V}{2c^2} \left| \phi_{\nu} \right\rangle^{-1} \left\langle \phi_{n,k} \right| \hat{p} \left| \phi_{\nu} \right\rangle. \]  

(3)

A major problem plaguing this operator is the fact that the presence of the potential in the inverse coulomb operator causes a lack of gauge invariance, i.e., if a constant is added to the potential this constant is not properly reproduced in the total energy. In our previous paper [11], we proposed to calculate the ZORA corrections separately for the atoms. To eliminate all dependence on the atomic coordinates both the potential and all matrix elements are calculated just for the atoms. Thus, we use

\[ (T^{ZORA})_{\mu \nu} = -\frac{1}{2} \left\langle \phi_{\mu} \right| p^2 \left| \phi_{\nu} \right\rangle - \frac{1}{2} \sum_{\lambda} \left\langle \phi_{\mu} \right| \hat{p} \left| \phi_{\lambda} \right\rangle \left\langle \phi_{\lambda} \right| \hat{p} \left| \phi_{\nu} \right\rangle 
\]

\[ - \sum_{n,k} \left\langle \phi_{\mu} \right| \hat{p} \left| \phi_{n,k} \right\rangle \left\langle \phi_{n,k} \right| \frac{2c^2 - V_{\text{Atom}}}{2c^2} \left| \phi_{\nu} \right\rangle^{-1} \left\langle \phi_{n,k} \right| \hat{p} \left| \phi_{\nu} \right\rangle \right\rangle_{\text{Atom}}. \]  

(4)

The relativistic corrections to the kinetic energy matrix elements may thus be calculated separately for each unique atom or even stored, requiring negligible computing time. Subsequently, they are only added to the kinetic energy integrals for basis functions that are both centered on the atom concerned. This way the influence of the potential of other atoms is completely eliminated, curing the gauge problem that results from this potential. Also, as the ZORA corrections move with the atoms, they have no other effect on the gradients than the change in the wave function due to the different kinetic energy operator. Thus, no special gradient-related terms need to be programmed. The reasoning that no extra terms enter our gradient expressions can be applied to the second derivatives as well. As the ZORA corrections move with the atoms no second derivatives of these corrections are required. The approach proved to be very accurate [11], as the elimination of the Gauge dependence well outweighs the minor effect of the other atoms on the atomic potential.

Other methods have been proposed to facilitate the calculation of gradients within the ZORA formalism. They include using a model potential [5], to allow analytic expressions for the gradients and applying corrections to the potentials to approximately eliminate the influence of the other atoms [6,12]. None of these methods, including our atomic ZORA, is gauge independent in a general sense. An extension of our atomic idea to the case of polarization abilities, for example, would entail simply ignoring the electric field in the evaluation of the ZORA correction.

Calculations

To illustrate the effectiveness of the method, we performed calculations on the vibrational states of Au, CsI, and UF₆. We present both Hartree–Fock and DFT (B3LYP [13, 14]) results. For UF₆ we also calculated vibrational modes using a pseudo-potential employing LanL2DZ, expecting little effect of the ZORA corrections. For a real-life application, we estimate the relevance of relativity for the vibrational spectrum of a V—O catalyst on a silica surface.

For Au and CsI, we use a basis employed previously [11]. For uranium, we employed an even-tempered basis set akin to a relativistic basis set of Koga et al. [15], whereas a DZVP basis was employed for fluorine. For the vanadium oxide umbrella structure [16], two basis sets (LanL2DZ and TZVP) were used.

The calculations were performed with the GAMESS-UK program [17]. In all cases, the ZORA corrections were calculated for Hartree–Fock atoms.

Results and Discussion

Table I compares analytical and finite-difference Hessians, calculated with a two-point approach (FORCE), for Au and CsI. The errors were similar
to those in nonrelativistic calculations and must be due to the limited accuracy of the FORCE calculation. The atomic ZORA corrections depend on the atomic density, since the electron repulsion is contained in the atomic potential V. For gold, the resulting iteration process took up to seven iterations to converge to $10^{-11}$, while the total energy reduced from $39720.120329$ to $39277.970266$ Hartree, compared with a nonrelativistic value of $35696.119946$. This suggests a considerable effect of the electron–electron repulsion on the final ZORA corrections. Although ZORA does show an improvement compared with experiment, the calculated frequencies are still significantly off. Comparison with more extended calculations [18] suggests that higher-order relativistic corrections and more extended correlation treatment is required for this weakly bonded system. The DK3 treatment in Ref. [18] raises the frequency by some $60$ cm$^{-1}$, compared with $40$ cm$^{-1}$ for ZORA, whereas CCSD(T) adds another $30$ cm$^{-1}$, compared with $20$ cm$^{-1}$ for DFT.

For the most relativistic molecule UF$_6$ (Table II), depending on the vibrational mode, the effects of adding DFT and adding relativity sometimes go in the same direction and sometimes cancel. The net effect is that each one on its own performs rather poorly, showing deviations from experiment [19, 20] ranging from $234$ cm$^{-1}$ (HF) and $113$ cm$^{-1}$ (B3LYP). Combining the DFT with the atomic ZORA gives a remarkable agreement with experiment, a deviation of only $12$ cm$^{-1}$. The pseudopotential calculations, named LanL2DZ, show quite acceptable frequencies in comparison with experiment; the ZORA corrections do not show improvement.

Calculations on the umbrella model [16] gave the results shown in Table III. From Table III, it is quite clear that the ZORA corrections have a small influence on the frequencies of the V=O stretch and O–O stretch in the peroxy group, depending of the basis set. As is to be expected, the LanL2DZ ecp basis set shows the smallest differences, since its core is already fitted to a relativistic one and cannot be changed by ZORA. The TZVP lowers the O–O vibration by $2$ cm$^{-1}$ and increases the V=O frequency by $4$ cm$^{-1}$. This basis places the O–O stretch at $940$ cm$^{-1}$, which compares well with the

### Table I

<table>
<thead>
<tr>
<th></th>
<th>Au$_2$</th>
<th></th>
<th>CsI</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R$</td>
<td>Hessian</td>
<td>FORCE</td>
<td>$R$</td>
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<tr>
<td>HF</td>
<td>2.879</td>
<td>104.63</td>
<td>104.67</td>
<td>3.563</td>
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<tr>
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<td>2.676</td>
<td>141.53</td>
<td>141.45</td>
<td>3.520</td>
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<tr>
<td>B3LYP</td>
<td>2.779</td>
<td>124.33</td>
<td>124.43</td>
<td>3.469</td>
</tr>
<tr>
<td>B3LYP-ZORA</td>
<td>2.621</td>
<td>154.92</td>
<td>154.78</td>
<td>3.435</td>
</tr>
<tr>
<td>Exp.</td>
<td>2.472</td>
<td>190.9</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* Experimental data for CsI [21] and Au$_2$ [22, 23]. Vibrations in cm$^{-1}$, and distances in Å.

### Table II

<table>
<thead>
<tr>
<th>UF$_6$</th>
<th>$R$</th>
<th>$a_{1g}$</th>
<th>$e_g$</th>
<th>$t_{1u}$</th>
<th>$t_{1u}$</th>
<th>$t_{2g}$</th>
<th>$t_{2u}$</th>
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<tr>
<td>HF</td>
<td>1.982</td>
<td>665</td>
<td>300</td>
<td>593</td>
<td>164</td>
<td>235</td>
<td>122</td>
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<tr>
<td>HF-ZORA</td>
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<td>740</td>
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<td>665</td>
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<td>145</td>
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<td>430</td>
<td>553</td>
<td>127</td>
<td>181</td>
<td>138</td>
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<tr>
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<td>546</td>
<td>628</td>
<td>181</td>
<td>194</td>
<td>146</td>
</tr>
<tr>
<td>B3LYP-LanL2DZ</td>
<td>2.019</td>
<td>632</td>
<td>527</td>
<td>620</td>
<td>171</td>
<td>188</td>
<td>146</td>
</tr>
<tr>
<td>B3LYP-LanL2DZ-ZORA</td>
<td>2.019</td>
<td>627</td>
<td>523</td>
<td>618</td>
<td>168</td>
<td>188</td>
<td>146</td>
</tr>
<tr>
<td>Exp.</td>
<td>1.999</td>
<td>676</td>
<td>534</td>
<td>626</td>
<td>186</td>
<td>200</td>
<td>143</td>
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</tbody>
</table>

* Vibrations in cm$^{-1}$, and distance in Å.
experimental value [16]. The difference between the LanL2DZ result and that produced with the TZVP basis indicates, that the lack of polarization functions is far more serious then any effect of relativity on the vibrations.

**Conclusion**

We show that the atomic ZORA approach is able to generate exact analytical Hessians. As the approach completely avoids the gauge problems associated with molecular ZORA calculations, the results are significantly more accurate than a molecular ZORA could be. Test calculations on UF₆ show remarkable agreement with experiment if both DFT and ZORA are enabled. The lack of relativistic effects in the standard calculations on vanadium oxides seems a justified approximation.

**ACKNOWLEDGEMENTS**

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**References**


**TABLE III**

Calculations on the vanadium oxide cluster.*

<table>
<thead>
<tr>
<th>Energy</th>
<th>LanL2DZ</th>
<th>TZVP</th>
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<tr>
<td>Atomic</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>−1286.1740379</td>
<td>−1287.4018909</td>
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<tr>
<td>Total</td>
<td>−1296.4430835</td>
<td>−1297.6638687</td>
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<tr>
<td>Vibrations</td>
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<td>O—O</td>
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<tr>
<td>V=O</td>
<td>1103.87</td>
<td>1103.95</td>
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</tbody>
</table>

* Energy in a.u., vibrations in cm⁻¹.