WILEY InterScience DISCOVER SOMETHING GREAT

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

J. H. VAN LENTHE,[1] J. N. J. VAN LINGEN[1,2]

[1]*Theoretical Chemistry Group,* Debye Institute, Department of Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

[2]*Inorganic Chemistry and Catalysis, Debye Institute, Department of Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Received 2 October 2005; accepted 9 December 2005
Published online 31 March 2006 in Wiley InterScience (www.interscience.wiley.com).
DOI 10.1002/qua.21047

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. 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:

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

Matrix elements of the kinetic energy operator thus become [9]:

Correspondence to: J. H. van Lenthe; e-mail: joop@chem.uu.nl
*Affiliated to Organic Chemistry and Catalysis.

$$(T^{\mathrm{ZORA}})_{\mu\nu} = \left\langle \phi_\mu \middle| p \cdot \frac{1}{2c^2 - V} \cdot p \middle| \phi_\nu \right\rangle, \qquad (2)$$

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

$$(T^{\mathrm{ZORA}})_{\mu\nu} = -\frac{1}{2}\langle \phi_\mu | p^2 | \phi_\nu \rangle - \frac{1}{2}\sum_\lambda \langle \phi_\mu | \vec{p} | \phi_\lambda \rangle \langle \phi_\lambda | \vec{p} | \phi_\nu \rangle + \frac{1}{2}\sum_{\kappa\lambda} \langle \phi_\mu | \vec{p} | \phi_\lambda \rangle \left\langle \phi_\lambda \middle| \frac{2c^2 - V}{2c^2} \middle| \phi_\kappa \right\rangle^{-1} \langle \phi_\kappa | \vec{p} | \phi_\nu \rangle. \qquad (3)$$

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

$$(T^{\mathrm{ZORA}})_{\mu\nu} = -\frac{1}{2}\langle \phi_\mu | p^2 | \phi_\nu \rangle - \frac{1}{2}\left\{ \sum_\lambda \langle \phi_\mu | \vec{p} | \phi_\lambda \rangle \langle \phi_\lambda | \vec{p} | \phi_\nu \rangle - \sum_{\kappa\lambda} \langle \phi_\mu | \vec{p} | \phi_\lambda \rangle \left\langle \phi_\lambda \middle| \frac{2c^2 - V_{\mathrm{Atom}}}{2c^2} \middle| \phi_\kappa \right\rangle^{-1} \langle \phi_\kappa | \vec{p} | \phi_\nu \rangle \right\}_{\mathrm{Atom}} \qquad (4)$$

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 polarizabilities, 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_2, CsI, and UF_6. We present both Hartree–Fock and DFT (B3LYP [13, 14]) results. For UF_6 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_2 and CsI. The errors were similar

TABLE I

Comparison of frequencies from analytical Hessians and 2-point force calculations for CsI and Au_2.*

	Au_2			CsI		
	R	Hessian	FORCE	*R*	Hessian	FORCE
HF	2.879	104.63	104.67	3.563	104.44	105.68
HF-ZORA	2.676	141.53	141.45	3.520	105.94	106.74
B3LYP	2.779	124.33	124.43	3.469	107.06	106.92
B3LYP-ZORA	2.621	154.92	154.78	3.435	108.09	108.18
Exp	2.472	190.9	—	—	113.9	—

* Experimental data for CsI [21] and Au_2 [22, 23]. Vibrations in cm^{-1}, and distances in Å.

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^{-6}, 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 peroxo 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 II

Calculated equilibrium distance and vibrational modes for UF_6 with experimental data [19, 20].*

UF_6	*R*	a_{1g}	e_g	t_{1u}	t_{1u}	t_{2g}	t_{2u}
HF	1.982	665	300	593	164	235	122
HF-ZORA	1.988	740	551	665	198	220	145
B3LYP	2.038	563	430	553	127	192	125
B3LYP-ZORA	2.012	664	546	628	181	194	138
B3LYP-LanL2DZ	2.019	632	527	620	171	188	146
B3LYP-LanL2DZ-ZORA	2.019	627	523	618	168	188	146
Exp.	1.999	676	534	626	186	200	143

* Vibrations in cm^{-1}, and distance in Å.

TABLE III
Calculations on the vanadium oxide cluster.*

	LanL2DZ		TZVP	
Energy	Nonrelativistic	ZORA	Nonrelativistic	ZORA
Atomic	−1286.1740379	−1287.4018909	−3299.1601219	−3311.4407690
Total	−1296.4430835	−1297.6638687	−3312.2795414	−3324.5615891
Vibrations				
O—O	912.37	913.05	944.56	941.63
V═O	1103.87	1103.95	1086.11	1089.98

* Energy in a.u., vibrations in cm^{-1}.

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 UF_6 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

The authors thank R. W. A. Havenith for critical reading of the manuscript.

References

1. Chang, C.; Pelissier, M.; Durand, P. Phys Scripta 1986, 34, 394.
2. Heully, J. L.; Lindgren, I.; Lindroth, E.; Lundqvist, S.; Maartensson-Pendrill, A. M. J Phys B 1986, 19, 2799.
3. Faas, S.; Snijders, J. G.; van Lenthe, J. H.; van Lenthe, E.; Baerends, E. J Chem Phys Lett 1995, 246, 632.
4. van Lenthe, E.; Baerends, E. J.; Snijders, J. G. J Chem Phys 1994, 101, 9783.
5. van Wüllen, C. J Chem Phys 1998, 109, 392.
6. Filatov, M.; Cremer, D. J Chem Phys 2005, 122, 44104.
7. Sadlej, A. J Coll Czech Chem Commun 2005, 70, 677.
8. Dirac, P. A. M. Proc R Soc (London) 1928, A118, 351.
9. van Lenthe, E.; van Leeuwen, R.; Baerends, E. J.; Snijders, J. G. Int J Quantum Chem 1996, 57, 281.
10. Faas, S.; Snijders, J. G.; van Lenthe, J. H. Prog Theor Chem Phys 2000, 2, 251.
11. van Lenthe, J. H.; Faas, S.; Snijders, J. G. Chem Phys Lett 2000, 328, 107.
12. van Lenthe, E.; Ehlers, A.; Baerends, E.-J. J Chem Phys 1999, 110, 8943.
13. Hertwig, R. H.; Koch, W. Chem Phys Lett 1997, 268, 345.
14. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. J Phys Chem 1994, 98, 11623.
15. Koga, T.; Tatewaki, H.; Matsuoka, O. J Chem Phys 2003, 119, 1279.
16. Gijzeman, O. L. J.; van Lingen, J. N. J.; van Lenthe, J. H.; Tinnemans, S. J.; Keller, D. E.; Weckhuysen, B. M. Chem Phys Lett 2004, 397, 277.
17. Guest, M. F.; Bush, I. J.; van Dam, H. J. J.; Sherwood, P.; Thomas, J. M. H.; van Lenthe, J. H.; Havenith, R. W. A.; Kendrick, J Mol Phys 2005, 103, 719.
18. Tsuchiya, T.; Abe, M.; Nakajima, T.; Hirao, K. J Chem Phys 2001, 115, 4463.
19. Hay, P. J.; Martin, R. L. J Chem Phys 1998, 109, 3875.
20. Schreckenbach, G.; Hay, P. J.; Martin, R. L. J Comp Chem 1999, 20, 70.
21. Konings, R. J. M.; Booij, A. S.; Cordfunke, E. H. P. Vibr Spect 1991, 2, 251.
22. Wang, F.; Liu, W. Chem Phys 2005, 311, 63.
23. Wang, X.; Wan, X.; Zhou, H.; Takami, S.; Kubo, M.; Miyamoto, A. J Mol Struct (Theochem) 2002, 579, 221.