



Relativistically corrected geometries obtained with analytical gradients: normalized elimination of the small component using an effective potential

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Abstract

For the quasi-relativistic normalized elimination of small component using an effective potential (NESC-EP) method, analytical energy gradients were developed, programmed, and implemented in a standard quantum chemical program package. NESC-EP with analytical gradients was applied to determine geometry, vibrational frequencies, and dissociation enthalpies of ferrocene, tungsten hexafluoride, and tungsten hexacarbonyl. Contrary to non-relativistic calculations and calculations carried out with RECPs for the same compounds, NESC-EP provided reliable molecular properties in good agreement with experiment. The computational power of NESC-EP results from the fact that reliable relativistic corrections are obtained at a cost level only slightly larger than that of a non-relativistic calculation. © 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

The necessity of relativistic corrections in quantum chemical calculations on systems with heavy atoms is well-known and a number of methods have been developed to provide an accurate account of relativistic effects on molecular properties [1–3]. However, there is still a need for quantum chemical methods that make it possible to include the most important relativistic corrections even into descriptions of relatively large molecules such as metallocenes, transition metal complexes with

more than one metal atom or enzymes containing a transition metal. Also, more and more quantum chemical work focuses on the third transition metal row and even on the actinides. We have recently developed a new quasi-relativistic method dubbed normalized elimination of small component using an effective potential (NESC-EP) [4], which compensates shortcomings of the low order approximation to the NESC approach [5] by the use of an effective potential. In follow-up work [6], we connected the NESC-EP approach with Kohn–Sham (KS) density functional theory (DFT) [7]. First benchmark calculations revealed that DFT–NESC-EP/B3LYP provides reasonable relativistic corrections, which compete with those of much more expensive methods on an equal footing [4,6].

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In this work, we report on an extension of our previous work aimed at routinely calculating molecular geometries with analytical energy derivatives. For this purpose, we develop the theory of analytical NESC gradients in Section 2 after shortly describing the basic theory of DFT–NESC-EP. In Section 3, we discuss the implementation of the newly developed gradients into a standard quantum chemical program package while in Section 4 applications with the new analytical approach are represented for some non-trivial examples.

2. Theory of NESC gradients

The NESC-EP method is based on the normalized elimination of the small component in the Dirac equation as developed by Dylla [5,8]. Utilizing substitution (1), which connects the small component Ψ_S of the Dirac wavefunction $\Psi_D = \begin{pmatrix} \Psi_L \\ \Psi_S \end{pmatrix}$ [9] with the so-called pseudo-large wavefunction Φ_L

$$\Psi_S = \frac{(\boldsymbol{\sigma} \cdot \mathbf{p})}{2mc} \Phi_L, \quad (1)$$

the one-electron Dirac equation can be modified to lead to:

$$\begin{aligned} \hat{T}\Phi_L + V\Psi_L &= E\Psi_L, \\ \hat{T}\Psi_L + \frac{1}{4m^2c^2}(\boldsymbol{\sigma} \cdot \mathbf{p})(V - E)(\boldsymbol{\sigma} \cdot \mathbf{p})\Phi_L &= \hat{T}\Phi_L, \end{aligned} \quad (2)$$

where \hat{T} is the kinetic energy operator

$$\hat{T} = \frac{\mathbf{p}^2}{2m} = \frac{(\boldsymbol{\sigma} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{p})}{2m}.$$

The elimination of Φ_L from Eq. (2), which is accomplished [8] with the help of the following relation:

$$\Phi_L = \hat{U}\Psi_L, \quad (3)$$

leads to the NESC equation

$$\begin{aligned} (\hat{T} - (\hat{I} - \hat{U}^\dagger)\hat{T}(\hat{I} - \hat{U}) + V \\ + \frac{1}{4m^2c^2}\hat{U}^\dagger(\boldsymbol{\sigma} \cdot \mathbf{p})V(\boldsymbol{\sigma} \cdot \mathbf{p})\hat{U})\Psi_L \\ = E\left(1 + \frac{\hat{U}^\dagger\hat{T}\hat{U}}{2mc^2}\right)\Psi_L. \end{aligned} \quad (4)$$

For a solution of the Dirac equation, the pseudo-large Φ_L and large Ψ_L components of the modified Dirac wavefunction are connected by [8],

$$(\boldsymbol{\sigma} \cdot \mathbf{p})\Phi_L = \left(1 + \frac{E - V}{2mc^2}\right)^{-1} (\boldsymbol{\sigma} \cdot \mathbf{p})\Psi_L, \quad (5)$$

which enables one to rewrite Eq. (4) as Eq. (6)

$$\begin{aligned} (\hat{T} + V + \frac{1}{4m^2c^2}(\boldsymbol{\sigma} \cdot \mathbf{p})V_{\text{eff}}(\boldsymbol{\sigma} \cdot \mathbf{p}))\Psi \\ = E\left(1 + \frac{\hat{T}}{2mc^2}\right)\Psi, \end{aligned} \quad (6)$$

$$\begin{aligned} V_{\text{eff}} &= Vw + E(1 - w) \\ &= \left(V + E\frac{(E - V)}{2mc^2}\right) / \left(1 + \frac{(E - V)}{2mc^2}\right), \end{aligned} \quad (7)$$

where w denotes the prefactor on the right-hand side (r.h.s.) of Eq. (5): $w = (1 + (E - V)/(2mc^2))^{-1}$ and the effective (energy-dependent) potential V_{eff} is given by Eq. (7). Eq. (6) is similar in its appearance to a low-order approximation (called NESC $\mathbf{U} = \mathbf{I}$ in [5]) of the exact Eq. (4). However, the effective potential V_{eff} absorbs implicitly higher-order corrections, which are not contained in the low-order approximation [4].

In our previous publications [4,6], it was proposed to model the energy-dependent effective potential V_{eff} in Eq. (6) with an energy-independent expression, which behaves at large distances from the nucleus as the usual Coulomb potential, however, remains finite at the position of nucleus. Thus, the one-electron NESC-EP (NESC with effective potential) equation is given by

$$\begin{aligned} (\hat{T} + V_{\text{Ne}} + \frac{1}{4m^2c^2}(\boldsymbol{\sigma} \cdot \mathbf{p})V'_{\text{Ne}}(\boldsymbol{\sigma} \cdot \mathbf{p}))\psi_i \\ = \epsilon_i\left(1 + \frac{\hat{T}}{2mc^2}\right)\psi_i, \end{aligned} \quad (8)$$

where the electron–nuclear attraction potential $V_{\text{Ne}}(\mathbf{r}_1) = \sum_n -Z_n/r_{1n}$ is replaced in the third term on the l.h.s. by potential.

$$V'_{\text{Ne}}(\mathbf{r}_1) = \sum_n^{all\ N} -\frac{Z_n}{r_{1n}} \text{erf}(r_{1n}/r_0(Z_n)). \quad (9)$$

In Eq. (9), $r_0(Z_n)$ is a cut-off radius specific for the n th nucleus and $r_{1n} = |\mathbf{r}_1 - \mathbf{r}_n|$ is the distance

between the n th nucleus and the electron position given by radius-vector \mathbf{r}_1 . The dependence of $r_0(Z_n)$ on the nuclear charge is given by the following equation [4]:

$$r_0(Z) = (a_0 + a_1 Z^{-1} + a_2 Z^{-2}) \frac{Z}{mc^2}, \quad (10)$$

with the coefficients $a_0 = -0.263188$, $a_1 = 106.016974$, $a_2 = 138.985999$ being based on a fit of the $1s_{1/2}$ eigenvalues of the Dirac equation [9] for H-like atomic ions. Expanding the one-electron wavefunctions (orbitals) ψ_i in terms of (non-orthogonal) basis set functions χ according to the following equation:

$$\psi_i = |\chi\rangle \mathbf{C}_i, \quad (11)$$

where $|\chi\rangle$ is the row-vector of basis functions, \mathbf{C}_i is the column-vector of expansion coefficients and using the one-electron relativistic approximation [10], the matrix form of the NESC-EP equation within the Kohn–Sham formalism is given by

$$\left((\mathbf{S}^{1/2})^\dagger (\mathbf{U}^{-1/2})^\dagger (\mathbf{T} + \mathbf{V} + \mathbf{W}) (\mathbf{U}^{-1/2}) (\mathbf{S}^{1/2}) + \mathbf{J} + \mathbf{V}_{\text{xc}} \right) \mathbf{C}_i = \mathbf{S} \mathbf{C}_i \epsilon_i, \quad (12)$$

where \mathbf{W} denotes the matrix of the operator

$$(\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{V'_{\text{Nc}}}{4m^2 c^2} (\boldsymbol{\sigma} \cdot \mathbf{p}),$$

the renormalization matrix \mathbf{U} is given by

$$\mathbf{U} = \mathbf{S} + \frac{1}{2mc^2} \mathbf{T}, \quad (13)$$

while \mathbf{J} and \mathbf{V}_{xc} are the matrices of the classical Coulomb repulsion operator and of the Kohn–Sham potential, respectively. The one-electron ($1\bar{e}$) approximation amounts to using the untransformed (non-relativistic) two-electron part of the many-body Hamiltonian in the relativistic case. Such an approximation corresponds to the neglect of a two-electron Darwin term and provides, as demonstrated in [4,10], reliable approximations to scalar relativistic effects. The total NESC-EP energy is given by the following equation:

$$\begin{aligned} E_{\text{NESC-EP}} &= E_{1\bar{e}} + E_C + E_{\text{xc}} \\ &= \text{tr} \left(\mathbf{P} \left((\mathbf{S}^{1/2})^\dagger (\mathbf{U}^{-1/2})^\dagger (\mathbf{V} + \mathbf{T} + \mathbf{W}) (\mathbf{U}^{-1/2}) (\mathbf{S}^{1/2}) \right) \right) + \frac{1}{2} \text{tr}(\mathbf{P}\mathbf{J}) + E_{\text{xc}}, \end{aligned} \quad (14)$$

where \mathbf{P} is the density matrix in the basis of functions χ

$$\mathbf{P} = \mathbf{C}\mathbf{n}\mathbf{C}^\dagger, \quad (15)$$

and E_{xc} is the usual KS exchange–correlation energy. In Eq. (15), \mathbf{n} is the diagonal matrix of orbital occupation numbers.

Eq. (14) differs from the corresponding non-relativistic expression only in the use of the relativistically corrected Hamiltonian for the one-electron ($1\bar{e}$) contribution to the total energy. Thus, the NESC-EP energy derivative with respect to nuclear coordinates will differ from the corresponding non-relativistic expression only in the one-electron contributions

$$\begin{aligned} \frac{\partial E_{1\bar{e}}}{\partial \lambda} &= \text{tr} \left(\mathbf{P} \left(\frac{\partial}{\partial \lambda} \left((\mathbf{S}^{1/2})^\dagger (\mathbf{U}^{-1/2})^\dagger \right. \right. \right. \\ &\quad \left. \left. \left. \times (\mathbf{V} + \mathbf{T} + \mathbf{W}) (\mathbf{U}^{-1/2}) (\mathbf{S}^{1/2}) \right) \right) \right) \\ &= \text{tr} \left(\mathbf{P} \left(\left(\frac{\partial}{\partial \lambda} \mathbf{G}^\dagger \right) \mathbf{H} \mathbf{G} + \mathbf{G}^\dagger \left(\frac{\partial}{\partial \lambda} \mathbf{H} \right) \mathbf{G} \right. \right. \\ &\quad \left. \left. + \mathbf{G}^\dagger \mathbf{H} \left(\frac{\partial}{\partial \lambda} \mathbf{G} \right) \right) \right) \\ &= \text{tr} \left(\left(\mathbf{G} \mathbf{P} \left(\frac{\partial}{\partial \lambda} \mathbf{G}^\dagger \right) + \left(\frac{\partial}{\partial \lambda} \mathbf{G} \right) \mathbf{P} \mathbf{G}^\dagger \right) \mathbf{H} \right) \\ &\quad + \text{tr} \left(\left(\mathbf{G} \mathbf{P} \mathbf{G}^\dagger \right) \left(\frac{\partial}{\partial \lambda} \mathbf{H} \right) \right) \\ &= \text{tr} \left(\left(\frac{\partial'}{\partial \lambda} \mathbf{P}' \right) \mathbf{H} \right) + \text{tr} \left(\mathbf{P}' \left(\frac{\partial}{\partial \lambda} \mathbf{H} \right) \right), \end{aligned} \quad (16)$$

where the \mathbf{G} , \mathbf{H} and \mathbf{P}' matrices are defined in Eqs. (17)–(19), respectively:

$$\mathbf{G} = \mathbf{U}^{-1/2} \mathbf{S}^{1/2}, \quad (17)$$

$$\mathbf{H} = \mathbf{V} + \mathbf{T} + \mathbf{W}, \quad (18)$$

$$\mathbf{P}' = \mathbf{G} \mathbf{P} \mathbf{G}^\dagger, \quad (19)$$

and the $\partial'/\partial\lambda$ symbol means that molecular integrals rather than orbital coefficients are to be differentiated.

The derivative of the \mathbf{H} matrix contains the derivatives of the electron–nuclear attraction ($(\partial/\partial\lambda)\mathbf{V}$) and kinetic energy integrals ($(\partial/\partial\lambda)\mathbf{T}$), which are easily available in standard quantum-chemical codes. In addition, the derivative of

matrix \mathbf{W} (see Eq. (12)) is required, which can be expressed in terms of the usual nuclear–electron attraction integrals as was recently discussed [4,6,11].

The derivative of the renormalization matrix \mathbf{G} with respect to a nuclear coordinate λ is expressed in Eq. (20) in terms of the derivatives of matrices $\mathbf{U}^{1/2}$ and $\mathbf{S}^{1/2}$.

$$\begin{aligned} \frac{\partial}{\partial \lambda} \mathbf{G} &= \frac{\partial}{\partial \lambda} (\mathbf{U}^{-1/2} \mathbf{S}^{1/2}) \\ &= \left(\frac{\partial}{\partial \lambda} \mathbf{U}^{-1/2} \right) \mathbf{S}^{1/2} + \mathbf{U}^{-1/2} \left(\frac{\partial}{\partial \lambda} \mathbf{S}^{1/2} \right) \\ &= -\mathbf{U}^{-1/2} \left(\frac{\partial}{\partial \lambda} \mathbf{U}^{1/2} \right) \mathbf{G} + \mathbf{U}^{-1/2} \left(\frac{\partial}{\partial \lambda} \mathbf{S}^{1/2} \right), \end{aligned} \quad (20)$$

where the identity

$$\frac{\partial}{\partial \lambda} \mathbf{A}^{-1} = -\mathbf{A}^{-1} \left(\frac{\partial}{\partial \lambda} \mathbf{A} \right) \mathbf{A}^{-1}$$

following from the differentiation of $\mathbf{A}^{-1} \mathbf{A} = \mathbf{I}$ is used.

The derivatives of the square root matrices can be taken [12] using the properties of eigenvalues and eigenvectors of a symmetric matrix \mathbf{A} , which can be diagonalized with the help of its eigenvectors \mathcal{C} according to $\mathbf{a} = \mathcal{C}^\dagger \mathbf{A} \mathcal{C}$. Differentiating the diagonal matrix \mathbf{a} and using the identity $\mathbf{A} = \mathcal{C} \mathbf{a} \mathcal{C}^\dagger$ one obtains the following equation:

$$\frac{\partial}{\partial \lambda} \mathbf{a} = \mathbf{a} \mathbf{R} - \mathbf{R} \mathbf{a} + \mathcal{C}^\dagger \left(\frac{\partial}{\partial \lambda} \mathbf{A} \right) \mathcal{C}, \quad (21)$$

where $\mathbf{R} = \mathcal{C}^\dagger ((\partial/\partial \lambda) \mathcal{C})$ is an antisymmetric matrix. The antisymmetry of \mathbf{R} follows from differentiation of the identity $\mathcal{C} \mathcal{C}^\dagger = \mathbf{I}$. The elements of the antisymmetric matrix \mathbf{R} can be calculated as follows:

$$\mathbf{R}_{ij} = \begin{cases} (a_j - a_i)^{-1} (\mathcal{C}^\dagger (\frac{\partial}{\partial \lambda} \mathbf{A}) \mathcal{C})_{ij} & i \neq j, \\ 0 & i = j, \end{cases} \quad (22)$$

which follows from Eq. (21) noting that the matrix \mathbf{a} is diagonal.

Analogously, for the square root of a diagonal matrix \mathbf{a} one obtains the following equation:

$$\frac{\partial}{\partial \lambda} \mathbf{a}^{1/2} = \mathbf{a}^{1/2} \mathbf{R} - \mathbf{R} \mathbf{a}^{1/2} + \mathcal{C}^\dagger \left(\frac{\partial}{\partial \lambda} \mathbf{A}^{1/2} \right) \mathcal{C}, \quad (23)$$

which after substituting Eq. (22) yields Eq. (24) for the derivative of the square root matrix $\mathbf{A}^{1/2}$.

$$\begin{aligned} & \left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \lambda} \mathbf{A}^{1/2} \right) \mathcal{C} \right)_{ij} \\ &= (a_j^{1/2} - a_i^{1/2}) \mathbf{R}_{ij} (a_j^{1/2} + a_i^{1/2})^{-1} \left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \lambda} \mathbf{A} \right) \mathcal{C} \right)_{ij}. \end{aligned} \quad (24)$$

The derivatives of matrices $\mathbf{U}^{1/2}$ and $\mathbf{S}^{1/2}$ can be calculated from Eq. (24). The derivatives of the overlap integrals which are necessary to calculate $(\partial/\partial \lambda) \mathbf{S}^{1/2}$ are available in the standard quantum-chemical programs, while the derivatives of the \mathbf{U} matrix are expressed in Eq. (25) in terms of the usual one-electron molecular integrals

$$\frac{\partial}{\partial \lambda} \mathbf{U} = \frac{\partial}{\partial \lambda} \mathbf{S} + \frac{1}{2mc^2} \frac{\partial}{\partial \lambda} \mathbf{T}. \quad (25)$$

3. Implementation and details of calculations

Analytical energy gradients for the NESC-EP method were programmed and implemented into the ab initio package COLOGNE 2002 [13] according to the procedure described in the previous Section. Appropriate tests were carried out by comparing analytical and numerical energy derivatives with regard to nuclear coordinates. After stepwise decrease of the increment value used in the numeric procedure analytic and numeric derivatives agreed within 10^{-5} – 10^{-6} hartree/bohr. Using convergence criteria of 5×10^{-4} hartree/bohr in the geometry optimization implies an accuracy in the calculated bond lengths of 10^{-4} Å.

The computational cost for setting up the analytic energy gradient requires not more than 20% of the SCF calculation of DFT–NESC-EP (for an average of 15 iteration cycles). Even better timings were found for larger molecules. Hence, we conclude that our implementation of analytic energy gradients for DFT–NESC-EP reduces the time needed for the total geometry optimization substantially and leads to accurate geometries.

DFT–NESC-EP calculations with the B3LYP functional [14] were carried out for ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$, tungsten hexafluoride WF_6 , and tung-

sten hexacarbonyl $W(CO)_6$. For comparison, non-relativistic DFT/B3LYP calculations on the same compounds were also performed. Calculations for ferrocene employed the contracted [8s6p4d1f] basis set of Wachters [15] for iron and Pople's 6-31G(d) basis set [16] for carbon and hydrogen. In the investigation of the tungsten complexes, a contracted [16s12p8d4f] basis for tungsten [17], the aug-cc-pVDZ basis for F, and the cc-pVDZ basis sets for C and O, respectively, were used [18].

For molecules $Fe(C_5H_5)_2$, WF_6 , and $W(CO)_6$, dissociation reactions were also investigated. Open-shell systems were calculated with the spin-unrestricted DFT approach. Energy differences were converted to enthalpy differences $\Delta H(298)$ at 298 K by calculating thermochemical corrections. For this purpose, vibrational frequencies were determined by numeric differentiation of analytic energy gradients with regard to nuclear coordinates applying the central difference formula with an increment of 0.001 Å. The spin-orbit corrections for the ground state energies of tungsten and fluorine and of WF_5 were taken from [19]. When calculating the dissociation enthalpy of ferrocene and the atomization enthalpy of tungsten hexafluoride, the basis set superposition error was taken into account with the help of the counterpoise correction method [20].

4. Results and discussion

Ferrocene was optimized imposing D_{5h} symmetry while for WF_6 and $W(CO)_6$ an O_h symmetry constraint was used. The products of the bond dissociation reaction: $WX_6 \rightarrow WX_5 + X$, namely WF_5 and $W(CO)_5$, possess C_{2v} and C_{4v} symmetry, respectively. Calculated geometries and dissociation energies are listed in Table 1 where the NESC-EP/B3LYP results are compared with the corresponding non-relativistic results. This comparison helps to elucidate the role of relativistic effects for the molecules considered. For ferrocene, the relativistic effect is expected to be relatively small [21]. The difference in the dissociation enthalpies of the reaction $Fe(C_5H_5)_2(^1A_{1g}) \rightarrow Fe^{2+}(^5D) + 2C_5H_5(^1A'_1)$ calculated at the quasi-relativistic and non-relativistic level of theory is 5.6 kcal/mol, which is

close to the 6 kcal/mol reported by Klopper and Lüthi [21] for ferrocene. Relativity results in a moderate shortening of Fe–C and Fe–cp (cp: center of pentagon of the cyclopentadienyl anion) distances by ca. 0.01 Å (NESC-EP: 2.068 and 1.673 Å; exp.: 2.058 and 1.660 Å [22]) while leaving the other bond lengths unchanged. This and the description of an isolated cyclopentadienyl anion, for which the quasi-relativistic and non-relativistic calculations yield identical geometries with C–C bond lengths of 1.414 Å, imply that the formalism described in the previous section works correctly and recovers the correct non-relativistic results in situations where relativity does not play a major role. Note, however, that the inclusion of relativity via the NESC-EP method brings the Fe–C and Fe–cp distances and the dissociation enthalpy (638 kcal/mol) in closer agreement with experimental data (635 ± 6 [21] and 636 ± 10 kcal/mol [23]).

For a heavier element such as tungsten, the effects of relativity are substantial with regard to both molecular geometry and dissociation enthalpies. In the case of WF_6 , the NESC-EP method yields excellent first and total bond dissociation enthalpies ($WF_6(^1A_{1g}) \rightarrow WF_5(^2B_2) + F(^2P)$: 729.5 kcal/mol; exp.: 729 ± 3 kcal/mol [19]; $WF_6(^1A_{1g}) \rightarrow W(^5D) + 6F(^2P)$: 123.6 kcal/mol; exp.: 121 ± 3 kcal/mol [19]) and an accurate molecular geometry (bond length WF: 1.837 vs. 1.832 [24] or 1.829 Å [25]). Relativity has a dramatic effect on the dissociation enthalpies of WF_6 and accounts for ca. 20% of the first bond dissociation enthalpy (123.6; non-rel.: 94.8 kcal/mol, Table 1). The results of the NESC-EP/B3LYP calculations can be compared with the results of B3LYP calculations based on the use of relativistic effective core potentials (RECP) reported by Dyal [19]. RECP/B3LYP performs poor for WF_6 as reflected by a WF bond length of 1.847 Å, an atomization enthalpy of 705 kcal/mol, and a first bond dissociation enthalpy of 110 kcal/mol [19]. For atomic tungsten, NESC-EP/B3LYP predicts correctly the $^5D(6s^25d^4)$ state to be the ground state with the $^7S(6s^15d^5)$ state lying 8.9 kcal/mol above the 5D state. The non-relativistic B3LYP and the RECP/B3LYP calculations incorrectly place the 7S state below the 5D state by 24.5 and 4.8 kcal/mol, respectively. The latter result shows that the RECP

Table 1
Results of molecular calculations

Parameter	NESC-EP	Non-relativistic	Exptl.	Other work
$\text{Fe}(\text{C}_5\text{H}_5)_2^{\text{a}}$				
$R_{\text{Fe-cp}}^{\text{b}}$ (Å)	1.673	1.683	$1.660 \pm 0.008^{\text{c}}$	
$R_{\text{Fe-C}}$ (Å)	2.068	2.076	$2.058 \pm 0.005^{\text{c}}$	
$R_{\text{C-C}}$ (Å)	1.428	1.428	$1.431 \pm 0.005^{\text{c}}$	
$R_{\text{C-H}}$ (Å)	1.082	1.082	$1.122 \pm 0.020^{\text{c}}$	
ΔH_{298}^0 (kcal/mol)	637.9	632.3	$635 \pm 6^{\text{e}}$; $636 \pm 10^{\text{f}}$	
WF_6^{g}				
$R_{\text{W-F}}$ (Å)	1.837	1.869	$1.832 \pm 0.003^{\text{h}}$; $1.829 \pm 0.002^{\text{i}}$	1.856 ^j ; 1.855 ^k
ΔH_{298}^0 (kcal/mol)	729.5	655.3	$729 \pm 3^{\text{m}}$	
ΔH_{298}^0 (kcal/mol)	123.6	94.8	$121 \pm 3^{\text{m}}$	
$\text{W}(\text{CO})_6^{\text{o}}$				
$R_{\text{W-C}}$ (Å)	2.051	2.103	$2.058 \pm 0.003^{\text{p}}$	2.060 ^j ; 2.052 ^k
$R_{\text{C-O}}$ (Å)	1.148	1.146	$1.148 \pm 0.0025^{\text{p}}$	
ΔH_{298}^0 (kcal/mol)	50.9	40.9	$46 \pm 2^{\text{r}}$	45.4 ^j ; 45.2

^a Calculations employed a [8s6p4d1f] basis [15] on Fe and 6-31G(d) basis [16] on C and H.

^b Metal-ring distance whereas the center of the cyclopentadienyl anion is used.

^c Taken from [22].

^d Enthalpy of the reaction: $\text{Fe}(\text{C}_5\text{H}_5)_2(^1\text{A}_{1g}) \rightarrow \text{Fe}^{2+}(^5\text{D}) + 2\text{C}_5\text{H}_5(^1\text{A}'_1)$.

^e From [21].

^f From [23].

^g Calculations employed a [16s12p8d4f] basis [17] on W and the aug-cc-pVDZ basis [18] on F.

^h From [24].

ⁱ From [25].

^j DPT/BP86 results from [28].

^k ZORA/BP86 results from [28].

^l Enthalpy of the reaction: $\text{WF}_6(^1\text{A}_{1g}) \rightarrow \text{W}(^5\text{D}) + 6\text{F}(^2\text{P})$.

^m From [19].

ⁿ Enthalpy of the reaction: $\text{WF}_6(^1\text{A}_{1g}) \rightarrow \text{WF}_5(^2\text{B}_2) + \text{F}(^2\text{P})$.

^o Calculations employed a [16s12p8d4f] basis [17] on W and the cc-pVDZ basis [18] on C and O.

^p From [27].

^q Enthalpy of the reaction: $\text{W}(\text{CO})_6(^1\text{A}_{1g}) \rightarrow \text{W}(\text{CO})_5(^1\text{A}_1) + \text{CO}(^1\Sigma)$.

^r From [26].

used in [19] (LANL2DZ) underestimates relativistic effects for the valence s- and d-orbitals of tungsten.

NESC-EP/B3LYP results for $\text{W}(\text{CO})_6$ are also in good agreement with experiment (see Table 1). Again, relativity contributes ca. 20% to the first bond dissociation enthalpy (non-rel.: 40.9; rel.: 50.9 kcal/mol, exp.: 46 ± 2 kcal/mol [26], Table 1). The metal–ligand bond length contraction ($2.103 - 2.051 = 0.052$ Å, exp.: 2.058 Å [27], Table 1) is even more pronounced for $\text{W}(\text{CO})_6$ than for WF_6 . The NESC-EP/B3LYP results are also in reasonable agreement with other all electron quasi-relativistic DFT calculations (see Table 1). Note, however,

that hybrid functionals such as B3LYP were not employed previously in all-electron quasi-relativistic calculations.

5. Conclusions

Analytical energy gradients were developed, programmed, and tested for the NESC-EP method. Their use leads to a substantial reduction of the computer time for geometry optimizations and vibrational frequency calculations with NESC-EP. Application of NESC-EP with analytical gradients confirms the computational power of the new

method, namely to obtain reliable relativistic corrections for molecular geometries at a cost level only slightly larger than that of a non-relativistic geometry optimization. In this way, quasi-relativistic calculations for relatively large molecules of interest in transition metal chemistry or biochemistry become accessible.

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