Calculation of electric properties using regular approximations to relativistic effects: The polarizabilities of RuO_4, OsO_4, and HsO_4 (Z=108)

Michael Filatov[a)] and Dieter Cremer

Department of Theoretical Chemistry, Göteborg University, Reutersgatan 2, S-41320 Göteborg, Sweden

Analytic expressions for the derivatives of the total molecular energy with respect to external electric field are derived within the regular approximation to the full four-component relativistic Hamiltonian and presented in matrix form suitable for implementation in standard quantum-chemical codes. Results of benchmark calculations using the *infinite-order regular approximation with modified metric* method are presented and discussed. The static electric dipole polarizabilities of group VIII metal tetroxides MO_4 for M=Ru, Os, Hs (Z=108) are studied with the help of second-order Møller–Plesset perturbation theory using the infinite-order regular approximation with modified metric Hamiltonian. The polarizabilities obtained vary in the sequence $RuO_4 > OsO_4 > HsO_4$, which is different from those obtained in other studies. However, it is in line with calculated $^1T_2 \leftarrow {}^1A_1$ excitation energies of the group VIII tetroxides, which provide a measure for the magnitude of their polarizabilities. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1580473]

I. INTRODUCTION

The electric dipole polarizability is a measure of the distortion of the overall atomic or molecular charge distribution by an external electric field.[1] The polarizability is a ubiquitous parameter that appears in many formulas for low-energy processes involving the valence electrons of atoms and molecules.[2] Knowledge of atomic and molecular polarizability is important in many areas of computational chemistry ranging from electron[3] and vibrational[4] spectroscopy to molecular modeling,[5] drug design,[6] and nano-technology.[7]

While the bulk of previous quantum-chemical calculations of polarizabilities focuses on compounds containing just light elements, there is now a growing interest in obtaining the electric response properties for inorganic and organometallic compounds containing heavy elements. Heavy atom compounds can only be correctly described by quantum-chemical methods including relativistic corrections. The core electrons of a heavy atom experience the largest effects of relativity, however, they have vanishingly small influence on to polarizability and other electric response properties of a molecule. Nevertheless these properties experience indirect relativistic effects via contraction or decontraction of valence and sub-valence electrons caused by relativity,[8–10] which can be significant. Thus, there is currently a substantial interest in developing computational methods capable of handling relativistic effects on molecular response properties.[11–16]

Although fully relativistic four-component calculations have been carried out[12,13,15,16] for a number of atoms and small molecules, the computational complexity of the rigorous four-component formalism based on the Dirac Hamiltonian[17] fuels the quest for simple yet reliable quasirelativistic methods. The methods based on the Douglas–Kroll (DK) transformation[18] as well as on a regular expansion[19,20] of the Dirac Hamiltonian have been established in recent years as cost effective alternatives to the full four-component formalism.

Recently, we have developed[21,22] a new algorithm for calculation of the matrix elements of the Hamiltonian within regular approximation (RA) approach, which can easily be applied in the context of basis set *ab initio* calculations. At variance with the Douglas–Kroll–Hess approach,[23] the new computational procedure is stable with respect to basis set reduction and produces reasonable results even with small basis sets.[22] For the purpose of uprooting the erroneous gauge dependence of the eigenvalues of the regular Hamiltonian,[19,20] a simple modification of the wave function metric within the infinite-order regular approximation (IORA)[20] method was suggested, which led to the IORA method with modified metric (IORAmm).[21,22] The IORAmm method[21,22] was successfully applied to study compounds of heavy elements within the context of *ab initio* wave function theory.[21,22,24,25]

The purpose of the present paper is to extend the formalism presented in our earlier works[21,22] so that it can be applied to the calculation of electric response properties. This development should provide the possibility of calculating relativistically corrected dipole moments, polarizabilities or hyperpolarizabilities of large molecules using just standard wave function *ab initio* techniques. It should be noted that previously the relativistic methods based on the regular approximation were used[26] almost exclusively within the context of density functional theory (DFT),[27] which often does not achieve a satisfactory level of accuracy when calculating electric response properties.[28]

Results of the current work will be presented in the following way. In Chapter II the IORAmm formalism is described briefly along with the formulas necessary to calculate the electric dipole moments and electric dipole polarizabil-

a)Electronic mail: filatov@theoc.gu.se

ities. Chapter III presents results of benchmark calculations performed for various atomic and molecular systems, for which the effect of relativity on static electric dipole polarizabilities varies from very small (noble gas atoms) to very large (mercury atom). The formalism developed is applied in Chapter IV to study electric dipole polarizabilities of group VIII metal tetroxides MO_4 for M=Ru, Os, Hs (Z=108). There is substantial interest in studying the properties of compounds containing super-heavy elements such as hassium (Hs).[29–33] The results of the present work provide a basis for a reassessment of the values of the polarizabilities of RuO_4 and HsO_4 calculated recently[30] at the level of relativistic DFT calculations.[34]

II. THEORY OF THE RELATIVISTIC DESCRIPTION OF ELECTRIC PROPERTIES

The energy of a molecule in a static uniform electric field $\mathbf{F}$ can be expanded as in Eq. (1) in terms of the field strength

$$E(\mathbf{F}) = E(0) + \frac{\partial E(\mathbf{F})}{\partial \mathbf{F}}\bigg|_{\mathbf{F}=0} \cdot \mathbf{F} + \frac{1}{2} \mathbf{F} \cdot \frac{\partial^2 E(\mathbf{F})}{\partial \mathbf{F} \partial \mathbf{F}}\bigg|_{\mathbf{F}=0} \cdot \mathbf{F} + \dots . \quad (1)$$

From this expansion the dipole moment is defined as in Eq. (2)

$$\mu = -\frac{\partial E(\mathbf{F})}{\partial \mathbf{F}}\bigg|_{\mathbf{F}=0}, \quad (2)$$

and the polarizability tensor as in Eq. (3)

$$\alpha = -\frac{\partial^2 E(\mathbf{F})}{\partial \mathbf{F} \partial \mathbf{F}}\bigg|_{\mathbf{F}=0}. \quad (3)$$

For convenience the experimentally measured polarizability is characterized by two parameters, isotropic polarizability (4)

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \quad (4)$$

and anisotropic polarizability (5)

$$\gamma^2 = \frac{1}{2}((\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2$$
$$+ 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2)), \quad (5)$$

which are invariant with respect to an orthogonal coordinate transformation.

A. The IORAmm methodology

The matrix IORAmm (or IORA) SCF equations in the one-electron ($1\bar{e}$) scalar-relativistic (SR) approximation[35] are given in Eq. (6)[21,22]

$$((\mathbf{S}^{1/2})^{\dagger}(\mathbf{U}^{-1/2})^{\dagger}(\mathbf{V}_n + \mathbf{T} + \mathbf{W})(\mathbf{U}^{-1/2})(\mathbf{S}^{1/2}) + \mathbf{J} - \mathbf{K})\mathbf{C}_i$$
$$= \mathbf{S}\mathbf{C}_i \boldsymbol{\epsilon}_i, \quad (6)$$

where $\mathbf{V}_n$ is the matrix of the electron–nuclear attraction integrals $\langle \chi_\mu | V_n | \chi_\nu \rangle$ (χ_μ: basis functions; V_n: Electron–nuclear attraction potential) and the matrix $\mathbf{U}$ is given by Eq. (7)

$$\mathbf{U} = \mathbf{S} + \frac{1}{2mc^2}(\mathbf{T} + a\mathbf{W} + b\mathbf{W}\mathbf{T}^{-1}\mathbf{W}), \quad (7)$$

(parameters a and b for IORA: $a=2$, $b=1$; for IORAmm: $a=3/2$, $b=1/2$). Matrix $\mathbf{T}$ is the usual kinetic energy matrix, $\mathbf{J}$ and $\mathbf{K}$ the Coulomb and exchange matrices, $\mathbf{S}$ the overlap matrix, $\mathbf{C}_i$ the column-vector of expansion coefficients, and ϵ_i the eigenvalue of the orbital ψ_i. The matrix $\mathbf{W}$ in Eqs. (6) and (7) is the solution of Eq. (8)

$$\mathbf{W} = \mathbf{W}_0 + \mathbf{W}_0 \mathbf{T}^{-1} \mathbf{W}, \quad (8)$$

which is given in Eq. (9)

$$\mathbf{W}^{-1} = \mathbf{W}_0^{-1} - \mathbf{T}^{-1}. \quad (9)$$

The matrix $\mathbf{W}_0$ in Eqs. (8) and (9) is calculated in the $1\bar{e}$ SR approximation according to Eq. (10)

$$\mathbf{W}_0 = \frac{1}{4m^2c^2} \langle \chi_\mu | \mathbf{p} V_n \cdot \mathbf{p} | \chi_\nu \rangle. \quad (10)$$

Note, that only the electron–nuclear attraction potential V_n is used in Eq. (10) and the electron–electron repulsion is treated nonrelativistically. This implies an assumption that the Foldy–Wouthuysen transformation[36] commutes with the electron–electron repulsion operator.[35] The solution of the IORAmm/IORA equation (6) approximates the true relativistic wave function in the Foldy–Wouthuysen representation.[20]

The total IORAmm/IORA SCF energy is given by Eq. (11)

$$E_{SCF} = tr(\tfrac{1}{2}\mathbf{P}(\mathbf{H} + \mathbf{F}))$$
$$= tr(\mathbf{P}((\mathbf{S}^{1/2})^{\dagger}(\mathbf{U}^{-1/2})^{\dagger}(\mathbf{V}_n + \mathbf{T} + \mathbf{W})(\mathbf{U}^{-1/2})(\mathbf{S}^{1/2})$$
$$+ \tfrac{1}{2}(\mathbf{J} - \mathbf{K}))), \quad (11)$$

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

$$\mathbf{P} = \mathbf{C}\mathbf{n}\mathbf{C}^{\dagger}. \quad (12)$$

In Eq. (12), $\mathbf{n}$ is the diagonal matrix of orbital occupation numbers. Eq. (11) differs from the corresponding nonrelativistic expression only in the use of the relativistically corrected one-electron Hamiltonian $\mathbf{H}_{1\bar{e}}$ for the calculation of the one-electron part to the total SCF energy.

When the molecular integrals in Eq. (11) depend on an external parameter λ, the first derivative of the self-consistent field (SCF) total energy with respect to the parameter λ is given in Eq. (13)[37]

$$\frac{\partial E}{\partial \lambda} = tr\left(\mathbf{P}\left(\frac{\partial}{\partial \lambda}\mathbf{H}\right)\right) + tr\left(\mathcal{W}\left(\frac{\partial}{\partial \lambda}\mathbf{S}\right)\right)$$
$$+ \frac{1}{2} tr\left(\mathbf{P}\left(\frac{\partial'}{\partial \lambda}(\mathbf{J} - \mathbf{K})\right)\right). \quad (13)$$

Here $\mathcal{W}$ is the energy-weighted density matrix

$$\mathcal{W} = \mathbf{C}\mathbf{n}\boldsymbol{\epsilon}\mathbf{C}^{\dagger}, \quad (14)$$

where $\boldsymbol{\epsilon}$ is the diagonal matrix of orbital energies. The prime at $\partial/\partial\lambda$ implies that only molecular two-electron integrals rather than density matrix elements (or orbital coefficients) have to be differentiated.

In an external electric field $\mathbf{F}$ with components F_α ($\alpha = x, y, z$), the potential $\mathbf{V}_n$ in Eq. (11) modifies to

$$V_n^{\mathbf{F}}(\mathbf{r}) = V_n(\mathbf{r}) + \mathbf{F} \cdot \mathbf{r}, \tag{15}$$

(given in atomic units with the electron charge incorporated into the definition of the potential). The other molecular integrals (overlap, kinetic energy, two-electron) remain unchanged. Thus, the first derivative with respect to a component F_α of the electric field reduces to

$$
\begin{aligned}
\frac{\partial E}{\partial F_\alpha} &= tr\left(\mathbf{P}\left(\frac{\partial \mathbf{H}}{\partial F_\alpha} \right) \right) \\
&= tr\left(\mathbf{P}\left(\frac{\partial}{\partial F_\alpha}((\mathbf{S}^{1/2})^\dagger (\mathbf{U}^{-1/2})^\dagger \right. \right. \\
&\quad \left. \left. \times (\mathbf{V}_n + \mathbf{T} + \mathbf{W})(\mathbf{U}^{-1/2})(\mathbf{S}^{1/2})) \right) \right) \\
&= tr\left(\mathbf{P}\left(\mathbf{G}^\dagger\left(\frac{\partial \mathbf{H}}{\partial F_\alpha} \right)\mathbf{G} \right) \right) \\
&\quad + tr\left(\mathbf{P}\left(\left(\frac{\partial \mathbf{G}^\dagger}{\partial F_\alpha} \right)\mathbf{HG} + \mathbf{G}^\dagger\mathbf{H}\left(\frac{\partial \mathbf{G}}{\partial F_\alpha} \right) \right) \right),
\end{aligned} \tag{16}
$$

where the matrices $\mathbf{G}$ and $\mathbf{H}$ are defined in Eqs. (17) and (18), respectively,

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

$$\mathbf{H} = \mathbf{V}_n + \mathbf{T} + \mathbf{W}. \tag{18}$$

The derivative of the $\mathbf{H}$ matrix with respect to a component of electric field F_α is given in Eq. (19)

$$
\begin{aligned}
\frac{\partial \mathbf{H}}{\partial F_\alpha} &= \frac{\partial \mathbf{V}_n}{\partial F_\alpha} + \mathbf{WW}_0^{-1}\left(\frac{\partial \mathbf{W}_0}{\partial F_\alpha} \right)\mathbf{W}_0^{-1}\mathbf{W} \\
&= \mathbf{R}_\alpha + \frac{1}{4m^2c^2}\mathbf{WW}_0^{-1}\mathbf{Q}_\alpha\mathbf{W}_0^{-1}\mathbf{W},
\end{aligned} \tag{19}
$$

where $\mathbf{R}_\alpha$ is the usual matrix of dipole integrals $\langle \chi_\mu | r_\alpha | \chi_\nu \rangle$ for the αth component of dipole moment and $\mathbf{Q}_\alpha$ is the matrix of the $\mathbf{p}r_\alpha \cdot \mathbf{p}$ operator. While the elements of the $\mathbf{Q}_\alpha$ matrix can easily be calculated using the usual dipole integrals routinely available in any nonrelativistic quantum-chemical code, its contribution to the derivative $\partial\mathbf{H}/\partial F_\alpha$ is expected to be negligible. Indeed, the elements of the $\mathbf{Q}_\alpha$ matrix depend on the gradient $\nabla\chi_\mu$ of the basis set functions, which is proportional to the orbital exponential factor and is large only in the core region. In the core region, the dipole integrals $\langle \chi_\mu | r_\alpha | \chi_\nu \rangle$ are small (typically $\sim 10^{-5} - 10^{-6}$ a.u.), 3 to 4 orders of magnitude smaller than in the valence and sub-valence region (typically $\sim 10^{-1} - 10^{-2}$ a.u.). Thus,

given that the elements $\langle \nabla\chi_\mu | r_\alpha | \nabla\chi_\nu \rangle$ of the $\mathbf{Q}_\alpha$ matrix are proportional to the dipole integrals and that the prefactor in front of the second term on the right hand side of Eq. (19) is $\sim 10^{-5}$, the contribution from this term can safely be neglected and only the first term can be retained in Eq. (19).

Using Eq. (36) of Ref. 22, the derivative of the renormalization matrix $\mathbf{G}$ in the second term on the right-hand side of Eq. (16) is given by Eq. (20)

$$\frac{\partial \mathbf{G}}{\partial F_\alpha} = -\mathbf{U}^{-1/2}\left(\frac{\partial \mathbf{U}^{1/2}}{\partial F_\alpha} \right)\mathbf{G}. \tag{20}$$

The derivative of the square-root of the matrix $\mathbf{U}$, Eq. (7), with respect to a field component F_α can be calculated using the eigenvectors $\mathcal{C}$ and eigenvalues u_i of the matrix $\mathbf{U}$ according to Eq. (21) [see also Eq. (43) of Ref. 22]

$$\left(\mathcal{C}^\dagger\left(\frac{\partial \mathbf{U}^{1/2}}{\partial F_\alpha} \right)\mathcal{C} \right)_{ij} = (\mathbf{u}_j^{1/2} + \mathbf{u}_i^{1/2})^{-1}\left(\mathcal{C}^\dagger\left(\frac{\partial \mathbf{U}}{\partial F_\alpha} \right)\mathcal{C} \right)_{ij}, \tag{21}$$

where the derivative of the matrix $\mathbf{U}$ with respect to a field component F_α is given in Eq. (22)

$$
\begin{aligned}
\frac{\partial \mathbf{U}}{\partial F_\alpha} &= \frac{1}{8m^3c^4}(a\mathbf{WW}_0^{-1}\mathbf{Q}_\alpha\mathbf{W}_0^{-1}\mathbf{W} \\
&\quad + b(\mathbf{WW}_0^{-1}\mathbf{Q}_\alpha\mathbf{W}_0^{-1}\mathbf{WT}^{-1}\mathbf{W} \\
&\quad + \mathbf{WT}^{-1}\mathbf{WW}_0^{-1}\mathbf{Q}_\alpha\mathbf{W}_0^{-1}\mathbf{W})).
\end{aligned} \tag{22}
$$

Since the eigenvalues of the $\mathbf{U}$ matrix, Eq. (7), are of the same order of magnitude as the eigenvalues of the overlap matrix (i.e., zeroth order in $1/c$), the derivatives $\partial\mathbf{U}^{1/2}/\partial F_\alpha$ and $\partial\mathbf{G}/\partial F_\alpha$ are of the order c^{-4}. Thus, the contribution from the second term on the right-hand side of Eq. (16) can be neglected compared to the contribution of the first term and Eq. (16) reduces to Eq. (23)

$$\mu_\alpha = -\frac{\partial E}{\partial F_\alpha} = -tr(\mathbf{P}(\mathbf{G}^\dagger\mathbf{R}_\alpha\mathbf{G})), \tag{23}$$

which implies that the dipole moment μ is calculated as the usual expectation value of the IORAmm/IORA wave function using the dipole integrals renormalized with matrix $\mathbf{G}$, which accounts for quasirelativistic correction to the wave function metric. The picture change effect on the dipole moment operator, which is contained in the second term in Eq. (19), is negligible (see also Refs. 11 and 38) and is not taken into account in Eq. (23).

Differentiating Eq. (16) with respect to electric field component F_β, one obtains Eq. (24) for the polarizability tensor α

$$
\begin{aligned}
\alpha_{\beta\alpha} = -\frac{\partial^2 E}{\partial F_\beta \partial F_\alpha} &= -tr\left(\left(\frac{\partial \mathbf{P}}{\partial F_\beta} \right)\left(\mathbf{G}^\dagger\left(\frac{\partial \mathbf{H}}{\partial F_\alpha} \right)\mathbf{G} \right) \right) - tr\left(\mathbf{P}\left(\mathbf{G}^\dagger\left(\frac{\partial^2 \mathbf{H}}{\partial F_\beta \partial F_\alpha} \right)\mathbf{G} \right) \right) - tr\left(\left(\frac{\partial \mathbf{P}}{\partial F_\beta} \right)\left(\left(\frac{\partial \mathbf{G}^\dagger}{\partial F_\alpha} \right)\mathbf{HG} + \mathbf{G}^\dagger\mathbf{H}\left(\frac{\partial \mathbf{G}}{\partial F_\alpha} \right) \right) \right) \\
&\quad - tr\left(\mathbf{P}\left(\left(\frac{\partial \mathbf{G}^\dagger}{\partial F_\beta} \right)\left(\frac{\partial \mathbf{H}}{\partial F_\alpha} \right) + \left(\frac{\partial \mathbf{G}^\dagger}{\partial F_\alpha} \right)\left(\frac{\partial \mathbf{H}}{\partial F_\beta} \right) \right)\mathbf{G} \right) - tr\left(\mathbf{PG}^\dagger\left(\left(\frac{\partial \mathbf{H}}{\partial F_\beta} \right)\left(\frac{\partial \mathbf{G}}{\partial F_\alpha} \right) + \left(\frac{\partial \mathbf{H}}{\partial F_\alpha} \right)\left(\frac{\partial \mathbf{G}}{\partial F_\beta} \right) \right) \right) \\
&\quad - tr\left(\mathbf{P}\left(\left(\frac{\partial^2 \mathbf{G}^\dagger}{\partial F_\beta \partial F_\alpha} \right)\mathbf{HG} + \mathbf{G}^\dagger\mathbf{H}\left(\frac{\partial^2 \mathbf{G}}{\partial F_\beta \partial F_\alpha} \right) \right) \right) - tr\left(\mathbf{P}\left(\left(\frac{\partial \mathbf{G}^\dagger}{\partial F_\beta} \right)\mathbf{H}\left(\frac{\partial \mathbf{G}}{\partial F_\alpha} \right) + \left(\frac{\partial \mathbf{G}^\dagger}{\partial F_\alpha} \right)\mathbf{H}\left(\frac{\partial \mathbf{G}}{\partial F_\beta} \right) \right) \right).
\end{aligned} \tag{24}
$$

With the help of Eqs. (19)–(22) it can be demonstrated that the third term on the right hand side (r.h.s.) of Eq. (24) is of the order $1/c^4$, the fourth and fifth terms both contain contributions of order $1/c^4$ and $1/c^6$, the sixth and seventh terms are of orders $1/c^6$ and $1/c^8$, respectively. Differentiating Eq. (19) with respect to a field component F_β Eq. (25) for the second derivative of the matrix $\mathbf{H}$ is derived

$$\frac{\partial^2 \mathbf{H}}{\partial F_\beta \partial F_\alpha} = \frac{1}{16 m^4 c^4} (\mathbf{W}\mathbf{W}_0^{-1}\mathbf{Q}_\alpha(\mathbf{W}_0^{-1}\mathbf{W}\mathbf{W}_0^{-1} - \mathbf{W}_0^{-1})$$
$$\times \mathbf{Q}_\beta \mathbf{W}_0^{-1}\mathbf{W} + \mathbf{W}\mathbf{W}_0^{-1}\mathbf{Q}_\beta(\mathbf{W}_0^{-1}\mathbf{W}\mathbf{W}_0^{-1} - \mathbf{W}_0^{-1})$$
$$\times \mathbf{Q}_\alpha \mathbf{W}_0^{-1}\mathbf{W}), \qquad (25)$$

which shows that the second term on the r.h.s. of Eq. (24) is of the order $1/c^4$. Because the interaction with an external electric field does not contain singular operators, the contributions of all terms except of the first one in Eq. (24) can safely be neglected. Furthermore, the first term contains contributions of both zeroth- and second-order in $1/c$ [see Eq. (19)] and only the zeroth-order terms make sizable contributions to the polarizability tensor. The second order terms ($\sim 1/c^2$), correspond to the picture change in the dipole moment operator and can be neglected as was demonstrated in the literature.[11,38] Thus, the expression for the polarizability tensor reduces to Eq. (26)

$$\alpha_{\beta\alpha} = -tr\left(\left(\frac{\partial \mathbf{P}}{\partial F_\beta}\right)(\mathbf{G}^\dagger \mathbf{R}_\alpha \mathbf{G})\right), \qquad (26)$$

which contains the renormalized dipole moment integrals and derivatives of the density matrix $\mathbf{P}$ calculated with the help of the usual coupled-perturbed (CP) equations[39] using the electric field as perturbation. Note, that the CP equations employ the renormalized dipole moment integrals as well.

Equation (26) could also be obtained by taking the derivative of the dipole moment vector given in Eq. (23) and neglecting contributions of the order $1/c^4$ resulting from the differentiation of matrix $\mathbf{G}$. However, we prefer to present the explicit derivation as given in Eq. (24) because this is needed when, e.g., the quadrupole shielding factor [to be used in nuclear magnetic resonance (NMR)] has to be calculated. While Eqs. (23) and (26) are applicable to the calculation of dipole moment and polarizability, the effects of a picture change neglected in these equations can become more important for other electric properties such as the electric field gradient (quadrupole shielding factor) at the nucleus.[38] In the latter case, at least the terms of the order $1/c^2$ should be retained in expressions for the derivatives of the total energy with respect to the nuclear quadrupole moment. However, as Eq. (19) shows, these additional terms can easily be evaluated using the standard nonrelativistic multipole integrals.

III. IMPLEMENTATION, BENCHMARK TESTS, AND CALCULATIONAL DETAILS

The computational scheme described in the previous section was programmed and implemented into the CO-LOGNE2003 suite of quantum-chemical programs.[40] The implementation is straightforward, because it requires only the renormalization of the dipole molecular integrals on the quasi-relativistic metric (17). Since only the one-electron part of the molecular Hamiltonian is modified in the IORAmm calculations, the cost of these calculations is essentially the same as the cost of the corresponding nonrelativistic calculations. Furthermore, the formalism described in the preceding section can be applied at the Hartree–Fock (HF) level as well as correlation corrected levels of theory such as Møller–Plesset many body perturbation theory, coupled cluster theory, etc.

A. Benchmark calculations

For the purpose of testing the effectiveness of the procedure described, IORAmm benchmark calculations of the static electric dipole polarizability were carried out for noble gas atoms He through Xe, for the mercury atom, and for hydrogen halides FH through AtH ($Z=85$) using a HF wave function. For comparison, nonrelativistic HF calculations were carried out for the same atoms and molecules.

For the calculation of the static electric dipole polarizabilities of the noble gas atoms the uncontracted TZV basis set of Ahlrichs was employed.[41] The original TZV basis set was amended by two sets of diffuse functions and a set of polarizing functions as described by Klopper et al.[42] Hence, the basis sets used for calculation of the polarizability of noble gas atoms He through Xe comprise the following functions: $He(7s4p)$, $Ne(13s8p4d)$, $Ar(16s11p5d)$, $Kr(19s15p8d3f)$, and $Xe(21s17p11d6f)$. Only cartesian Gaussian-type primitive functions are employed.

The results of IORAmm/HF and nonrelativistic HF calculations are presented in Table I where they are compared with the results of the Dirac–Fock (DF),[17,43] direct perturbation theory (DPT)[44] and scaled ZORA[19] calculations taken from the work of Klopper et al.[42] The literature data were obtained with the same basis sets, but using numeric differentiation of the total atomic energy with respect to the external electric field.[42] The comparison reveals that the IORAmm results reproduce closely the results of DF and other quasirelativistic calculations. The effect of a picture change in the dipole moment operators does not show up as is obvious from the comparison of the IORAmm results where this effect is neglected, with the DPT and scaled ZORA results, which take this effect into account.

The overall effect of relativity on the polarizabilities of the noble gas atoms is weak, which is consistent with minor relativistic effects observed for the atomic valence p-orbitals.[8–10] Much stronger influence of relativity should be expected in situations where valence s-orbitals, which experience a substantial relativistic shift, are distorted by an external electric field as in the case of the mercury atom. The enormous relativistic effect on the static electric dipole polarizability of mercury is well established.[45–47] According to numeric DF calculations,[45] the polarizability of mercury changes from 80 to 43 bohr^3 upon inclusion of relativity. In the last line of Table I, the results of nonrelativistic HF and IORAmm/HF calculations are compared with the literature data.[45–47] The $[17s14p9d8f]$ basis set on mercury employed in the present work was constructed from the $(19s14p10d5f)$ Hg basis set of Gropen[48] in the following

TABLE I. Static electric dipole polarizabilities α (bohr^3) of noble gas atoms and the Hg atom. Calculations employ the uncontracted and augmented Ahlrichs TZV basis set (Ref. 41) unless noted otherwise.

Atom	Hartree–Fock[a]	IORAmm[a]	Dirac–Fock[b]	Other methods[b]
He	1.316 75	1.316 57	1.316 55	1.316 55;[c] 1.31655[d]
Ne	2.3598	2.3625	2.3625	2.3624;[c] 2.3624[d]
Ar	10.707	10.719	10.720	10.718;[c] 10.718[d]
Kr	15.63	15.59	15.64	15.61;[c] 15.61[d]
Xe	26.6	26.3	26.5	26.3;[c] 26.3[d]
Hg	80.0[e]	43.1[e]	43.0[f]	44.9;[g] 45.26[h]

[a]This work.
[b]Taken from Ref. 42.
[c]Direct perturbation theory. Taken from Ref. 42.
[d]Scaled ZORA. Taken from Ref. 42.
[e]Calculated with a $[17s14p9d8f]$ basis set (see text for details).
[f]Numeric Dirac–Fock value from Ref. 45.
[g]Relativistic RPA value from Ref. 46.
[h]DK-HF value from Ref. 47.

way. In the original basis set the most diffuse set of primitive d-type Gaussian type functions (GTFs) was removed to avoid orthogonality problems. One s-type, four p- and d-type, and three f-type sets of diffuse GTFs were added in a well tempered sequence using an exponent ratio of 2.5. Five s-type GTFs (#4 to #8 in the original basis) were contracted to two s-type basis functions according to a 3/2 pattern. The eight inner p-type GTFs were contracted to three p-type basis functions using a 3/3/2 contraction pattern. Seven tight d-type sets of GTFs were contracted according to a 3/2/1/2 pattern and the four most tight f-type sets of GTFs were contracted to one set. The resulting $[17s14p9d8f]$ basis set is sufficiently flexible to be compared with the results of numeric DF calculations. The data listed in Table I show that in the nonrelativistic HF calculation the exact value[45] of 80 bohr^3 is indeed reproduced. The IORAmm/HF result is in a very good accord with the exact relativistic value[45] and is in fact better than that obtained in the relativistic random phase approximation[46] and DK[47] calculations.

The calculations of dipole moment and static electric dipole polarizability of hydrogen halides were carried out with modified basis sets designed by Sadlej[49] for the calculation of molecular electric properties. The original basis sets for elements H$(6s4p)[3s2p]$, F$(10s6p4d)[5s3p2d]$, Cl$(14s10p4d)[2s5p2d]$, Br$(15s12p9d4f)[9s7p4d2f]$, and I$(19s15p12d4f)[11s9p6d2f]$ were used in their uncontracted form. The basis set for At was only partially contracted in the following way. Starting from the completely uncontracted basis set, the five innermost s-type primitive GTFs were contracted to one s-type basis function using the coefficients for the first s-AO calculated with the original uncontracted basis set. The same was done for the five innermost p-type GTFs, the four innermost d-type GTFs, and the two innermost f-type GTFs, which were contracted to one p-, one d- and one f-set of basis functions. Because of orthogonality problems, four s-type GTFs (#13 to #16 in the original set) were replaced with three s-type GTFs with exponents obtained from that of the s-type GTF #12 in a well-tempered sequence with ratio 2.5. The most diffuse s-type GTF and the d-type GTF #11 from the original set were dropped because of orthogonality problems. The resulting $[14s13p10d4f]$ ba-

TABLE II. Dipole moments μ (bohr electron) and static electric dipole polarizabilities α (bohr^3) of the hydrogen halides XH. All calculations employ the uncontracted pVTZ basis of Sadlej. (Ref. 45) Interatomic distances are taken from Ref. 15.

Method	Reference	μ_z[a]	$\alpha_\perp$[b]	$\alpha_\parallel$[c]	$\bar{\alpha}$[d]
			FH		
Hartree–Fock	This work	−0.7684	4.52	5.87	4.97
IORAmm/HF	This work	−0.7665	4.52	5.88	4.97
TD-HF	15	−0.7682	4.51	5.87	4.96
TD-DK[e]	15	−0.7668	4.52	5.88	4.97
TD-DHF	15	−0.7667	4.52	5.88	4.97
			ClH		
Hartree–Fock	This work	−0.4849	16.20	18.37	16.92
IORAmm/HF	This work	−0.4783	16.23	18.40	16.96
TD-HF	15	−0.4849	16.20	18.37	16.92
TD-DK[e]	15	−0.4799	16.23	18.39	16.95
TD-DHF	15	−0.4794	16.23	18.40	16.96
			BrH		
Hartree–Fock	This work	−0.3788	22.58	25.05	23.40
IORAmm/HF	This work	−0.3550	22.58	25.06	23.41
TD-HF	15	−0.3823	22.57	25.06	23.40
TD-DK[e]	15	−0.3638	22.58	25.07	23.41
TD-DHF	15	−0.3610	22.65	25.15	23.48
			IH		
Hartree–Fock	This work	−0.2563	34.55	37.68	35.59
IORAmm/HF	This work	−0.2005	34.24	37.40	35.30
TD-HF	15	−0.2553	35.59	37.71	35.63
TD-DK[e]	15	−0.2100	34.31	37.45	35.36
TD-DHF	15	−0.1971	34.43	37.69	35.52
			AtH		
Hartree–Fock	This work	−0.1956	41.86	45.14	42.95
IORAmm/HF	This work	−0.0297	40.78	43.87	41.81
TD-HF	15	−0.1944	41.94	45.17	43.02
TD-DK[e]	15	−0.0538	40.77	43.82	41.78
TD-DHF	15	+0.0621	42.15	46.00	43.43

[a]z-Component of dipole moment. Molecule is oriented along z-axis with the hydrogen atom at the origin.
[b]Transverse component of polarizability.
[c]Longitudinal component of polarizability.
[d]Average polarizability.
[e]TD-HF results with spin-averaged Douglas–Kroll one-electron Hamiltonian.

sis set was used for the At calculations rather than the uncontracted $(20s17p14d5f)$ basis set. It should be noted that the contractions of GTFs were only applied in the deep core region so that they do not affect the calculation of dipole moment and polarizability, which depend primarily on the valence and sub-valence orbitals.

The results of IORAmm/HF and nonrelativistic HF calculations of the dipole moment and the static electric dipole polarizability of hydrogen halides FH through AtH are listed in Table II along with the results of recent time-dependent HF (TD-HF), time-dependent Douglas–Kroll (TD-DK), and time-dependent Dirac–Hartree–Fock (TD-DHF) calculations by Norman *et al.*[15] performed for the same properties. As it has already been noted by Norman *et al.*,[15] relativistic effects on the polarizability are extremely weak, just of the order of a few percent. Furthermore, the spin–orbit interaction does not play an important role for the polarizability of closed-shell species[15] and the SR approximation, adopted here and by Norman *et al.* for the TD-DK method,[15] is sufficient for describing this property correctly.

Generally, there is a reasonably good match between the

J. Chem. Phys., Vol. 119, No. 3, 15 July 2003

Polarizabilities of RuO₄, OsO₄, and HsO₄   1417

TABLE III. Static electric dipole polarizabilities α (bohr³) of tetroxides of group VIII elements Ru, Os, and Hs (Z=108).

Method	Parameter	RuO₄[a]	OsO₄[b]	HsO₄[c]
HF	$\bar{\alpha}$/bohr³	49.41	48.46	47.42
	$q/\bar{e}$[d]	+2.33	+2.56	+3.27
IORAmm/HF	$\bar{\alpha}$/bohr³	48.78	46.63	43.06
	$q/\bar{e}$	+2.41	+2.74	+3.48
MP2	$\bar{\alpha}$/bohr³	59.91	58.91	57.09
	$q/\bar{e}$	+1.57	+1.83	+2.48
IORAmm/MP2	$\bar{\alpha}$/bohr³	59.20	56.57	51.04
	$q/\bar{e}$	+1.65	+1.96	+2.78
Expt.	$\bar{\alpha}$/bohr³	⋯	55.13[e]	⋯
	r_{M-O}/Å	1.706±0.003[f]	1.714±0.003[g]	⋯

[a]Calculated at the experimental M–O bond length of 1.706 Å. The IORAmm/MP2 value is 1.716 Å.
[b]Calculated at the experimental M–O bond length of 1.714 Å. The IORAmm/MP2 value is 1.743 Å.
[c]Calculated at the IORAmm/MP2 bond length of 1.726 Å.
[d]NBO charge at the metal atom.
[e]From Ref. 57.
[f]From Ref. 51.
[g]From Ref. 52.

results of IORAmm/HF and TD-DHF calculations. The only exception concerns the sign of the dipole moment of AtH, which should be positive (according to the fact that the electronegativity of At is smaller than that of H) as correctly described by TD-DHF, however, is negative at the IORAmm/HF level of theory (Table II). TD-HF and TD-DK theory make much larger errors in this respect and considering that the dipole moment is rather small both at the IORAmm/HF and the TD-DHF level of theory, the former result is acceptable. In total, the results of the atomic and molecular benchmark calculations show that the IORAmm formalism described in the previous chapter is capable of reproducing with reasonable accuracy both weak and strong effects of relativity on dipole moment and polarizability.

B. Group VIII metal tetroxides

IORAmm was applied to study the static electric dipole polarizability of group VIII metal tetroxides MO₄ for M=Ru, Os, and Hs (Z=108). The calculations were carried out at the HF as well as at the second-order Møller–Plesset many-body perturbational theory (MP2)[50] levels. In the MP2 calculations, all valence electrons of the oxygen atoms, the $4s$-, $4p$-, $4d$-, and $5s$-electrons of ruthenium, the $4f$-, $5s$-, $5p$-, $5d$-, and $6s$-electrons of osmium, and the $5f$-, $6s$-, $6p$-, $6d$-, and $7s$-electrons of hassium were correlated. The experimental molecular geometries (T$_d$ point group) were used where available (RuO₄[51] and OsO₄[52]), otherwise the molecular geometry was optimized with the IORAmm/MP2 method utilizing the analytic energy gradients developed recently.[22] For comparison with the available experimental data (see Table III), the molecular geometries of RuO₄ and OsO₄ were also optimized with IORAmm/MP2 that resulted in the M–O bond lengths of 1.716 Å (calculated) vs 1.706±0.003 Å[51] (experimental) for RuO₄ and of 1.743 Å vs 1.714±0.003 Å[52] for OsO₄. The calculated polarizabilities were analyzed with the help of the excitation energies from the ground $^1A_1$ state of MO₄ to the lowest excited singlet states calculated with

the help of the configuration interaction with single substitutions (CIS) method.[53] The natural bond orbital (NBO) analysis[54] was employed to determine reliable atomic charges in MO₄ species.

In the calculations, the augmented correlation-consistent aug-cc-pVTZ basis set of Dunning[55] was employed for oxygen. For ruthenium, the block-contracted [$14s9p6d1f$] basis set derived from the ($17s12p8d$) basis set of Gropen[48] was employed. The original contracted basis set was decontracted and augmented with two diffuse primitive GTFs of s-type, two diffuse GTFs of p-type, and two diffuse GTFs of d-type in a well-tempered sequence (exponent ratio: 2.5). One f-type GTF was added with an exponent obtained with the formula[42] $\zeta_l = \zeta_{l-1}(2l+3)/(2l+1)$ (l: angular momentum quantum number) from the most diffuse exponent in the d-set. Then, eight s-type GTFs (#2 to #9 in the original set) were contracted to three s-sets according to a contraction pattern of 4/2/2 using the contraction coefficients of the first, second, and third s-orbitals obtained for Ru with the original basis set. The eight innermost p-type GTFs were contracted to three p-sets (contraction pattern 4/2/2) using the coefficients from the first three p-orbitals also obtained with the original set. Finally, the six most tight d-type GTFs were contracted to two sets according to a 4/2 contraction pattern utilizing the contraction coefficients taken from the $3d$-orbitals calculated the original set.

For osmium, a block-contracted [$16s12p9d3f$] basis set was derived from a ($19s14p10d5f$) basis set[48] in the following way. The most diffuse s-type GTF and the most diffuse d-type GTF were removed because of orthogonality problems (resulting from the use of Cartesian d-functions). Three s-type, four p- and d-type, and one f-type diffuse GTFs were added in a well-tempered sequence employing the ratio of 2.5. Then, eight s-type GTFs (#4 to #11 in the original set) were contracted to three s-type basis functions (contraction pattern: 4/2/2) using the contraction coefficients from the first three s-orbitals calculated for Os with the original basis set. The nine innermost p-type GTFs were contracted to three p-type functions (contraction pattern 4/3/2) using the contraction coefficients of the first three p-orbitals obtained with the original set. The six most tight d-type GTFs were contracted to two d-functions (contraction pattern 4/2) employing the contraction coefficients of the d-orbitals of the original set. Finally, the four innermost f-type GTFs were contracted to one f-orbital.

For hassium (Z=108), a block-contracted [$17s13p11d7f$] basis set was derived from a ($28s21p18d13f$) basis set developed by Tatewaki[56] for lawrencium (Z=103). The five most diffuse s-type GTFs were removed because of orthogonality problems and replaced by five GTFs with exponents derived in a well-tempered sequence (ratio: 2.5). Two diffuse p-type GTFs, two diffuse d-type GTFs, and two diffuse f-type GTFs were added in a well-tempered sequence (ratio: 2.5). Sixteen s-type GTFs (#7 to #22 in the original set) were contracted to five s-functions (contraction pattern: 4/4/3/3/2) using the coefficients from the first five s-orbitals calculated for Hs with the original set. Fifteen p-type GTFs were contracted to five p-functions (contraction pattern 2/5/3/3/2) using the coeffi-

TABLE IV. Low-energy electronic dipole transition energies (in eV) and dimensionless oscillator strengths in tetroxides of group VIII elements Ru, Os, and Hs (Z=108).

Molecule	Method	$A - {}^1T_2 \leftarrow X - {}^1A_1$	$B - {}^1T_2 \leftarrow X - {}^1A_1$	$C - {}^1T_2 \leftarrow X - {}^1A_1$
RuO_4[a]	CIS	4.05/0.0079	5.37/0.0215	5.84/0.0001
	IORAmm/CIS	4.28/0.0102	5.71/0.0274	6.05/0.0008
OsO_4[b]	CIS	4.66/0.0043	6.06/0.0334	6.97/0.0000
	IORAmm/CIS	5.38/0.0116	6.96/0.0504	7.48/0.0071
HsO_4[c]	CIS	6.06/0.0004	7.64/0.0534	9.04/0.0001
	IORAmm/CIS	8.14/0.0193	9.68/0.0832	10.31/0.0495

[a]Calculated at the experimental M–O bond length of 1.706 Å.
[b]Calculated at the experimental M–O bond length of 1.714 Å.
[c]Calculated at the IORAmm/MP2 bond length of 1.726 Å.

cients of the $2p$-, $2p$, $3p$-, $4p$-, and the $5p$-orbital obtained with the original set. Fourteen d-type GTFs were contracted to five d-functions (contraction pattern 2/3/3/3/3) utilizing the coefficients taken from the $3d$-, $3d$-, $3d$-, $4d$-, and $5d$-orbital of the original set. Twelve f-type GTFs were contracted to four f-functions (contraction pattern 4/3/3/2) employing the coefficients of the $4f$-, $4f$-, $5f$-, and $5f$-orbital of the original set. Although the basis set used for hassium was not specifically optimized for this element, the contraction scheme applied results in a basis set, which is sufficiently flexible in the valence and sub-valence regions to guarantee the calculation of reliable electric response properties.

IV. RESULTS AND DISCUSSION

Static electric dipole polarizabilities of group VIII metal tetroxides calculated with the quasirelativistic IORAmm as well as the nonrelativistic HF and MP2 methods are listed in Table III. The only experimentally known value is the polarizability of OsO_4 of 55.13 bohr[3].[57] The IORAmm/MP2 value of 56.57 bohr[3] is in a reasonable agreement with experiment, whereas HF (both quasirelativistic and nonrelativistic) underestimates substantially the polarizability. However, all methods employed (correlated, uncorrelated, quasirelativistic, nonrelativistic) suggest an ordering of the polarizabilities of group VIII metal tetroxides according to $RuO_4 > OsO_4 > HsO_4$. The origin of such an ordering can be traced back to variations of the dipole electronic transition energies from the ground $^1A_1$ state to excited $^1T_2$ states, which are presented in Table IV. These excitation energies play an important role for the static electric dipole polarizability as reflected by Eq. (27)[2]

$$\bar{\alpha} = \sum_{k \neq 0} \frac{f_{0k}}{(\Delta E_{0k})^2}, \tag{27}$$

where f_{0k} is the dimensionless oscillator strength and ΔE_{0k} the corresponding excitation energy (given in hartrees). Although the CIS method,[53] which is employed to study the excitation energies, does not include dynamic electron correlation corrections and, therefore, cannot be expected to yield accurate excitation energies, it provides the qualitative trends of the excitation energies reasonably well (see Table IV). The data in Table IV show that the lowest $^1T_2 \leftarrow {}^1A_1$ excitation energy increases in the sequence $RuO_4 < OsO_4 < HsO_4$. At the nonrelativistic level, this increase is associated with in-

creasing ionicity of M–O bonds in the tetroxides (see NBO metal charges in Table III). The highest occupied molecular orbitals of MO_4 are the ligand-centered t_1- and t_2-symmetric orbitals, whereas the metal d-orbitals (e- and t_2-symmetric) are empty. As the ligand charge becomes more negative in the sequence $RuO_4 < OsO_4 < HsO_4$ (see Table III), the empty metal d-orbitals are increasingly destabilized in the electric field of ligands. Relativity adds to this trend destabilizing the metal d-orbitals further.[8–10] This is reflected in the $^1T_2 \leftarrow {}^1A_1$ excitation energies presented in Table IV. The relativistic blue shift (with respect to the nonrelativistic values) of the excitation energies is especially pronounced in HsO_4 where it reaches ~ 2 eV for the lowest dipole transitions. Hence, the dipole polarizabilities of MO_4 calculated with IORAmm are smaller than the nonrelativistic polarizabilities.

The quasirelativistic calculations in the present work are performed at the SR level, neglecting all spin-dependent relativistic effects of which the most important are spin–orbit (SO) interactions. The inclusion of SO interactions results in splitting of the atomic d-levels into $d_{5/2}$- and $d_{3/2}$-sublevels. However, the magnitude of this splitting is smaller than the SR destabilization of d-orbitals with respect to the nonrelativistic values. For example, the four-component DHF calculations of Malli[32] yielded 4.35 eV for the SR destabilization of $6d$-orbitals of Hs, whereas the SO splitting between $6d_{5/2}$- and $6d_{3/2}$-orbitals was only 1.74 eV (2.22 and 1.05 eV for SR-destabilization and SO-splitting of Os, respectively).[32] The SO interaction, which is missing in the IORAmm calculations, could have resulted in the splitting of dipole excitation energies around the values reported in Table IV into lines shifted upward and downward in energy, such that the overall effect of the SO interactions on the polarizabilities should be minimal and should not overturn the trend obtained in the SR IORAmm calculations.

In general, the static electric dipole polarizabilities obtained in the IORAmm calculations appear to be more accurate than the theoretical values obtained previously with the help of relativistic DFT calculations.[30] Despite the use of the full four-component formalism, the values of 43.73 (RuO_4), 40.22 (OsO_4), and 42.24 bohr[3] (HsO_4) obtained by Pershina et $al.$[30] are far too low compared to the experimental data available.[57] Apart from a large underestimation of the polarizability of OsO_4, the relativistic DFT calculations predict a trend $RuO_4 > OsO_4 < HsO_4$, which differs from that obtained in the present work. Given that conventional density func-

tionals have not an exceptionally good record when calculating electric response properties,[28] the results of Pershina et al.[30] can not be considered reliable.

Yet another trend in polarizabilities of MO_4 (M=Ru, Os, Hs) was obtained by Düllmann et al.,[31] who used for OsO_4 the experimental value of 55.13 bohr[3], for HsO_4 the value (57.15 bohr[3]) from relativistic DFT calculations of Pershina et al.[30] corrected for the difference between the calculated and experimental polarizabilities of OsO_4, and for RuO_4 a value (53.45±1.01 bohr[3]) obtained by extrapolation from polarizability of OsO_4 assuming that the polarizability is proportional to the molar volume. Thus, a trend $RuO_4 < OsO_4 < HsO_4$ precisely opposite to that of the present work was obtained. However, such a trend, which is based on both the results of unreliable calculations and a questionable extrapolation procedure[58] rather than direct measurements, can hardly be considered as being reliable.

The static electric dipole polarizabilities obtained by Pershina et al.[30] and Düllmann et al.[31] were used to estimate the adsorption enthalpies of metal tetroxides on the quartz surface under the assumption that only physical adsorption (due to dispersion forces) takes place[59] and that the MO_4 molecules behave like spherically symmetric atoms. Because the experimental adsorption enthalpies vary in the order $RuO_4 < OsO_4 < HsO_4$[33] and because the energy of physical adsorption of a spherically symmetric atom is roughly proportional to electric dipole polarizability,[59] the same ordering of the polarizabilities of MO_4 was advocated by Düllmann et al.[31] and Pershina et al.[30] However, the results of the present work suggest that the trend in the measured adsorption enthalpies has to be rationalized on the basis of a more detailed model for adsorption, which takes into account molecular structure rather than just the polarizabilities and dispersion forces of the MO_4 molecules. In particular, the bond ionicity should be considered because it relates with electrostatic interactions possible between MO_4 and quartz surface. It should be noted that the metal charge in MO_4 correlates nicely with the adsorption enthalpies as has been established in earlier work by Pershina[29] and by Malli,[32] respectively. In the present investigation, the NBO charges on metal obtained with the help of IORAmm/MP2 calculations (see Table III) are in line with the trend in the observed adsorption enthalpies.

IV. CONCLUSIONS

Within the regular approximation to the full four-component relativistic Hamiltonian, the analytic expressions for the derivatives of the total molecular energy with respect to an external electric field are derived and presented in matrix form suitable for implementation in standard quantum-chemical codes. The formalism developed is tested in *ab initio* calculations of electric dipole moments and static electric dipole polarizabilities for a number of compounds containing heavy elements. The benchmark calculations demonstrate that the formalism presented enables one to obtain for compounds containing heavy elements results, which closely match the exact four-component relativistic results at essentially the same price as that of conventional nonrelativistic calculations. It is gratifying that with the use of the

IORAmm method both very weak and very strong effects of relativity on atomic and molecular polarizabilities can be successfully described.

The formalism developed was applied to study the static electric dipole polarizabilities of group VIII metal tetroxides MO_4 for M=Ru, Os, Hs (Z=108). The polarizabilities obtained at the IORAmm/MP2 level of theory decrease in the sequence $RuO_4 > OsO_4 > HsO_4$, which is different from those obtained in earlier studies based on relativistic DFT calculations.[30,31] On the basis of the trend obtained in the present work, it is suggested to reconsider dispersion models of adsorption of MO_4 on a quartz surface in favor of more elaborate models which consider both electrostatic and dispersion interactions. For example, the adsorption enthalpy correlates well with the M–O bond ionicity suggesting an electrostatic component of adsorption.

[1] C. J. E. Boettcher, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1973).
[2] T. M. Miller and B. Bederson, Adv. At. Mol. Phys. **13**, 1 (1977).
[3] A. H. de Vries, P. Th. van Duijnen, R. W. Zijlstra, and M. Swart, J. Electron Spectrosc. Relat. Phenom. **86**, 49 (1997).
[4] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular vibrations: The Theory of Infrared and Raman Vibrational spectra* (Dover, New York, 1980).
[5] S. W. Rick and S. J. Stuart, Rev. Comput. Chem. **18**, 89 (2002).
[6] U. Norinder and T. Österberg, Perspect. Drug Discovery Des. **19**, 1 (2000).
[7] M. Broyer, R. Antonine, E. Benichou, I. Compagnon, P. Dugourd, and D. Rayane, Comp. Rend. Phys. **3**, 301 (2002).
[8] P. Pyykkö, Chem. Rev. **88**, 563 (1988); **97**, 597 (1997).
[9] W. H. E. Schwarz, in *Theoretical Models of Chemical Bonding. Part 2. The concept of the Chemical Bond*, edited by Z. B. Maksić (Springer-Verlag, Berlin, 1990), p. 593.
[10] J. Almlöf and O. Gropen, in *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (VCH, New York, 1996), Vol. 8, p. 203.
[11] V. Kellö, A. J. Sadlej, and B. A. Hess, J. Chem. Phys. **105**, 1995 (1996).
[12] L. Visscher, T. Saue, and J. Oddershede, Chem. Phys. Lett. **274**, 181 (1997).
[13] A. Derevianko, W. R. Johnson, M. S. Safronova, and J. F. Babb, Phys. Rev. Lett. **82**, 3589 (1999).
[14] K. G. Dyall, Int. J. Quantum Chem. **78**, 412 (2000).
[15] P. Norman, B. Schimmelpfennig, K. Ruud, H. J. Aa. Jensen, and H. Ågren, J. Chem. Phys. **116**, 6914 (2002).
[16] M. Pecul and A. Rizzo, Chem. Phys. Lett. **370**, 578 (2003).
[17] P. A. M. Dirac, Proc. R. Soc. London, Ser. A **117**, 610 (1928).
[18] M. Douglas and N. M. Kroll, Ann. Phys. (N.Y.) **82**, 89 (1974); B. A. Hess, Phys. Rev. A **32**, 756 (1985); **33**, 3742 (1986).
[19] Ch. Chang, M. Pélissier, and P. Durand, Phys. Scr. **34**, 394 (1986); J.-L. Heully, I. Lindgren, E. Lindroth, S. Lundqvist, and A.-M. Mårtensson-Pendrill, J. Phys. B **19**, 2799 (1986); E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 9783 (1994).
[20] K. G. Dyall and E. van Lenthe, J. Chem. Phys. **111**, 1366 (1999).
[21] M. Filatov, Chem. Phys. Lett. **365**, 222 (2002).
[22] M. Filatov and D. Cremer, J. Chem. Phys. **118**, 6741 (2003).
[23] A. Wolf, M. Reiher, and B. A. Hess, J. Chem. Phys. **117**, 9215 (2002).
[24] M. Filatov and D. Cremer, Phys. Chem. Chem. Phys. **5**, 1103 (2003).
[25] M. Filatov, Chem. Phys. Lett. **373**, 131 (2003).
[26] See, e.g., G. T. Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S.

J. A. van Gisbergen, J. G. Snijders, and T. Ziegler, J. Comput. Chem. **22**, 931 (2001), and references cited therein.

[27] W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).

[28] S. J. A. van Gisbergen, V. P. Osinga, O. V. Gritsenko, R. van Leeuwen, J. G. Snijders, and E. J. Baerends, J. Chem. Phys. **105**, 3142 (1996); B. Champagne, E. A. Perpète, S. J. A. van Gisbergen, E. J. Baerends, J. G. Snijders, C. Soubra-Ghaoui, K. A. Robins, B. Kirtman, *ibid.* **109**, 10489 (1998); B. Champagne, E. A. Perpète, D. Jacquemin, S. J. A. van Gisbergen, E. J. Baerends, C. Soubra-Ghaoui, K. A. Robins, B. Kirtman, J. Phys. Chem. A **104**, 4755 (2000).

[29] V. Pershina, Chem. Rev. **96**, 1977 (1996), and references cited therein.

[30] V. Pershina, T. Bastug, B. Fricke, and S. Varga, J. Chem. Phys. **115**, 792 (2001).

[31] C. E. Düllmann, B. Eichler, R. Eichler, H. W. Gäggeler, and A. Türler, J. Phys. Chem. B **106**, 6679 (2002).

[32] G. L. Malli, J. Chem. Phys. **117**, 10441 (2002).

[33] C. E. Düllmann *et al.*, Nature (London) **418**, 859 (2002).

[34] A. K. Rajagopal, J. Phys. C **11**, L943 (1978); A. H. MacDonald and S. H. Vosko, *ibid.* **12**, 2977 (1979); E. Engel, S. Keller, and R. M. Dreizler, Phys. Rev. A **53**, 1367 (1996).

[35] K. G. Dyall, J. Chem. Phys. **115**, 9136 (2001); K. G. Dyall, J. Comput. Chem. **23**, 786 (2002); M. Filatov and D. Cremer, Theo. Chem. Acc. **108**, 168 (2002).

[36] L. L. Foldy and S. A. Wouthuysen, Phys. Rev. **78**, 29 (1950).

[37] P. Pulay, Mol. Phys. **17**, 197 (1969); J. Chem. Phys. **78**, 5043 (1983).

[38] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **105**, 2373 (1996); V. Kellö and A. J. Sadlej, Int. J. Quantum Chem. **68**, 159 (1998).

[39] C. E. Dykstra, *Ab Initio Calculation of the Structures and Properties of Molecules* (Elsevier, Amsterdam, 1988).

[40] E. Kraka, J. Gräfenstein, J. Gauss, M. Filatov, V. Polo, A. Wu, F. Reichel, L. Olsson, Z. Konkoli, Z. He, and D. Cremer, COLOGNE 2003, Göteborg University, Göteborg, 2003.

[41] R. Ahlrichs and K. May, Phys. Chem. Chem. Phys. **2**, 943 (2000).

[42] W. Klopper, E. van Lenthe, and A. C. Hennum, J. Chem. Phys. **113**, 9957 (2000).

[43] B. Swirles, Proc. R. Soc. London, Ser. A **152**, 625 (1935).

[44] W. Kutzelnigg, Phys. Rev. A **54**, 1183 (1996), and references cited therein.

[45] J. P. Desclaux, L. Laaksonen, and P. Pyykkö, J. Phys. B **14**, 419 (1981).

[46] D. Kolb, W. R. Johnson, and P. Shorer, Phys. Rev. A **26**, 19 (1982).

[47] C. F. Kunz, C. Hattig, and B. A. Hess, Mol. Phys. **89**, 139 (1996).

[48] O. Gropen, J. Comput. Chem. **8**, 982 (1987).

[49] A. J. Sadlej, Collect. Czech. Chem. Commun. **53**, 1995 (1988); A. J. Sadlej, Theor. Chim. Acta **79**, 123 (1991); **81**, 45 (1991); **81**, 339 (1992); **83**, 351 (1992).

[50] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934); for a recent review, see D. Cremer, in *Encyclopedia of Computational Chemistry*, edited by P. V. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner (Wiley, Chichester, UK, 1998), Vol. 3, p. 1706.

[51] B. Krebs and K.-D. Hasse, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **32**, 1334 (1976).

[52] S. Díaz-Moreno and D. T. Bowron, Organometallics **22**, 390 (2003).

[53] J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. J. Frisch, J. Phys. Chem. **96**, 135 (1992).

[54] J. E. Carpenter and F. Weinhold, J. Mol. Struct.: THEOCHEM **46**, 41 (1988); A. E. Reed, R. B. Weinstock, and F. Weinhold, J. Chem. Phys. **83**, 735 (1985); A. E. Reed, L. A. Curtiss, and F. Weinhold, Phys. Rev. **88**, 899 (1988).

[55] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).

[56] T. Koga, H. Tatewaki, and T. Shimazaki, Chem. Phys. Lett. **328**, 473 (2000).

[57] *CRC Handbook of Chemistry and Physics*, 76th ed. 1995–1996, edited by D. R. Lide (CRC, Boca Raton, FL, 1996), pp. 10–197.

[58] For discussion of relationship between polarizability and volume see, P. Politzer, P. Jin, and J. S. Murray, J. Chem. Phys. **117**, 8197 (2002), and references cited therein.

[59] A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, 1976).