

Analytic energy derivatives for regular approximations of relativistic effects applicable to methods with and without correlation corrections

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Analytic expressions are derived for the evaluation of derivatives of the total molecular energy with respect to external parameters (nuclear coordinates, external electric fields, etc.) within the relativistic regular approximation. The presented formalism employs the spectral resolution of the identity avoiding, however, the explicit use of an auxiliary basis set in the calculation of the matrix elements of the regular relativistic Hamiltonian. The final formulas for the total energy and energy derivatives are presented in matrix form suitable for implementation into standard quantum chemical packages. Results of benchmark calculations for gold containing diatomic molecules and for xenone hexafluoride performed at the Hartree–Fock and various correlation corrected levels of theory are presented and discussed. © 2003 American Institute of Physics.

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I. INTRODUCTION

Currently, it is well recognized that the incorporation of relativistic effects into quantum-chemical calculations is extremely important for the correct description of chemical bonding in compounds with heavy elements.^{1–3} Computational complexity of the rigorous four-component computational procedure, which is orders of magnitude more expensive than the standard nonrelativistic procedure, prompts researchers to seek low-cost yet accurate approximate approaches. In recent years, the methods based on a regular expansion^{4–12} of the Dirac Hamiltonian¹³ as well as on the Douglas–Kroll transformation^{14–16} have been established as cost effective alternatives to the full four-component formalism. The zeroth-order (ZORA)^{6,7} and infinite-order (IORA)⁸ regular approximations lead to a two- or one-component variationally stable Hamiltonian, which is capable of describing the valence and subvalence electronic shells of heavy elements with a remarkable accuracy.^{6,7,11,12}

The methods based on the regular approximation are almost exclusively used within the context of density functional theory.¹⁷ Applications within the context of wave function theory are relatively rare.^{9–12} This is probably due to difficulties in calculating the matrix elements of the ZORA or IORA Hamiltonian with the standard basis sets employed in quantum chemistry.¹⁸ The regular-approximated Hamiltonian contains the full molecular potential in the denominator, which makes it impossible to express its matrix elements in a closed algebraic form. Thus, one sticks to the use of numeric quadratures, which is a customary approach within density functional theory (DFT) but is quite inefficient in conventional wave-function-based methods. A straightforward use of the spectral resolution of the identity (RI), suggested by Faas *et al.*,⁹ requires a huge auxiliary basis set to provide the required accuracy.

Recently, an efficient way of calculating the matrix elements of the ZORA and IORA Hamiltonians was developed.¹⁹ Although the new computational procedure relies on the RI technique, the explicit use of an auxiliary basis set is avoided and the matrix elements of the quasirelativistic Hamiltonian can be obtained at essentially the same cost as in the nonrelativistic case. It is important to note that the new computational procedure is quite insensitive to the size of a basis and provides reasonable results even with small basis sets.

Yet another hurdle for the rosy prospect of applying the relativistic regular approximation is its gauge dependence problem.^{6–8,11,12} When a constant shift is added to the potential, the ZORA or IORA eigenenergy does not shift by exactly the same amount. This results in an appearance of non-physical forces between the nuclei and makes the direct calculation of energy differences impossible. Hence, one should be content with certain modifications of the original formalism, which are aimed at reducing the gauge dependence.^{6,7,18} The IORA Hamiltonian, which differs from the ZORA Hamiltonian by renormalization using a quasirelativistic metric, experiences a much weaker gauge dependence problem.⁸ This feature encouraged a simple modification of the original IORA quasirelativistic metric, which reduces the gauge dependence even further.¹⁹ Atomic and molecular calculations with the new method, dubbed IORamm (IORA with modified metric), have shown that the residual gauge dependence does not affect the geometry of molecules containing heavy elements.¹⁹ When calculating the energy differences (e.g., binding energies), the effect of the residual gauge dependence (usually no more than a few kilocalories per mole) can be taken into account with the help of a simple procedure¹⁹ similar to the counterpoise correction for basis set superposition errors.²⁰

The purpose of the present paper is to develop further the formalism of Ref. 19 and to present analytic expressions for the evaluation of molecular energy derivatives with re-

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spect to external parameters. Once such formulas are derived, they can be applied to the calculation of the analytic energy gradient (first derivative with respect to nuclear coordinates) needed for geometry optimization or of other energy-related properties, such as dipole moment, electric dipole polarizability, etc. In Sec. II a brief survey of the IORamm method and of the computational technique used for the evaluation of the Hamiltonian matrix elements is presented along with the expressions for the energy derivatives. The formalism developed is applied to the calculation of the spectroscopic parameters of diatomic molecules containing gold atoms as well as to the calculation of xenone hexafluoride. Section III describes the implementation of analytical energy derivatives into a standard quantum chemical program and details of the calculations. The results of the calculations performed at the self-consistent field (SCF) and at the MP n ($n=2-4$) levels of theory are presented in Sec. IV. Section V concludes the paper.

II. THEORY

The derivation of approximate relativistic theories normally starts with the transformation of the full four-component Dirac Hamiltonian¹³ to a two-component form using for example the Foldy–Wouthuysen (FW) formalism.^{21,22} Then, spin-dependent relativistic effects are neglected to obtain a one-component (spin-free) theory.

Making the regular approximation for the exact FW operator \hat{X} by⁸

$$\hat{X} = \frac{c}{2mc^2 - V} (\boldsymbol{\sigma} \cdot \mathbf{p}), \quad (1)$$

where $\boldsymbol{\sigma}$ is the vector of the Pauli matrices $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$,²³ $\mathbf{p} = -i\hbar\nabla$ is the momentum operator, m is the rest mass of electron and c is the velocity of light, leads to the IORA Hamiltonian

$$\begin{aligned} \hat{H}^{\text{IORA}} = & \frac{1}{\sqrt{1 + (\boldsymbol{\sigma} \cdot \mathbf{p}) (c^2 / (2mc^2 - V)^2) (\boldsymbol{\sigma} \cdot \mathbf{p})}} \\ & \times \left(V + (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{c^2}{2mc^2 - V} (\boldsymbol{\sigma} \cdot \mathbf{p}) \right) \\ & \times \frac{1}{\sqrt{1 + (\boldsymbol{\sigma} \cdot \mathbf{p}) (c^2 / (2cm^2 - V)^2) (\boldsymbol{\sigma} \cdot \mathbf{p})}}, \quad (2) \end{aligned}$$

which is referred to as the infinite-order regular approximation (IORA).⁸ The IORA Hamiltonian has been proposed in Ref. 8 where it has been shown that \hat{H}^{IORA} is bounded from below on the same domain of the potentials V as the zeroth-order regular approximated (ZORA) Hamiltonian.⁶ Thus, \hat{H}^{IORA} can be used in quasivariational calculations.

A serious disadvantage of the ZORA and IORA Hamiltonians is their lack of gauge invariance.⁶⁻⁸ If a constant shift Δ is added to the potential,

$$V_\Delta = V + \Delta, \quad (3)$$

then the eigenvalues of a gauge invariant method should be shifted by exactly the same amount Δ . For IORA, the gauge shift error (GSE) is⁸

$$E_0^{\text{IORA}} - E_\Delta^{\text{IORA}} + \Delta \approx - \frac{(E_0^{\text{IORA}})^2 \Delta}{4m^2 c^4}, \quad (4)$$

which is small compared to the gauge dependence of ZORA.⁶

$$E_0^{\text{ZORA}} - E_\Delta^{\text{ZORA}} + \Delta \approx \frac{E_0^{\text{ZORA}} \Delta}{2mc^2}, \quad (5)$$

however still large enough to induce a considerable distortion of the molecular geometry if the method is applied in molecular calculations.^{11,12}

A modification to the original normalization operator \hat{U} ,

$$\hat{U} = \frac{1}{\sqrt{1 + (\boldsymbol{\sigma} \cdot \mathbf{p}) (c^2 / (2mc^2 - V)^2) (\boldsymbol{\sigma} \cdot \mathbf{p})}}, \quad (6)$$

of the IORA Hamiltonian, which reduces considerably the gauge dependence of its eigenenergy, was proposed in Ref. 19. The IORamm Hamiltonian reads

$$\begin{aligned} \hat{H}^{\text{IORamm}} = & \frac{1}{\sqrt{1 + (1/2) (\boldsymbol{\sigma} \cdot \mathbf{p}) ((1/2mc^2) c^2 / (2mc^2 - V) + (c^2 / (2mc^2 - V)^2)) (\boldsymbol{\sigma} \cdot \mathbf{p})}} \left(V + (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{c^2}{2mc^2 - V} (\boldsymbol{\sigma} \cdot \mathbf{p}) \right) \\ & \times \frac{1}{\sqrt{1 + (1/2) (\boldsymbol{\sigma} \cdot \mathbf{p}) ((1/2mc^2) c^2 / (2mc^2 - V) + (c^2 / (2mc^2 - V)^2)) (\boldsymbol{\sigma} \cdot \mathbf{p})}}. \quad (7) \end{aligned}$$

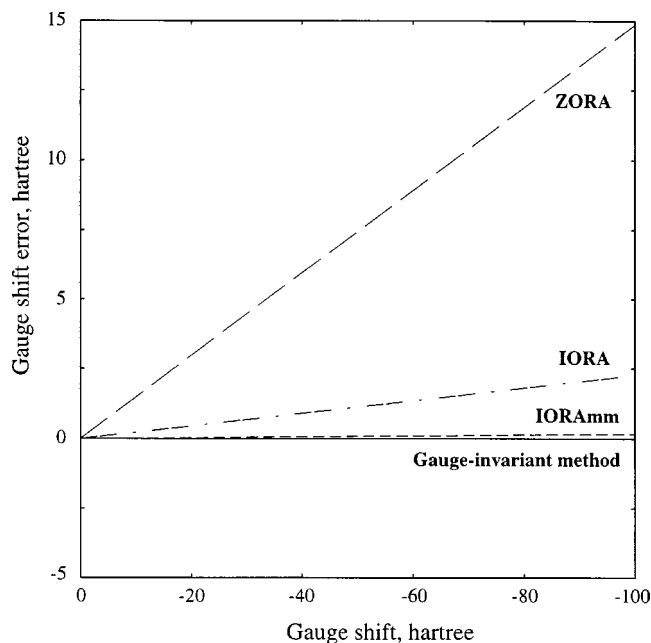


FIG. 1. Gauge shift error $E_0 - E_\Delta + \Delta$ obtained for the ground state energy of U^{91+} as a function of the gauge shift Δ for ZORA (long-dashed line), IORA (dot-dashed line), IORAm (short-dashed line), and the gauge-invariant method (solid line).

As has been demonstrated in atomic and molecular calculations,¹⁹ the IORAm Hamiltonian has a gauge dependence, which is approximately two orders of magnitude weaker than that of IORA. Hence, the IORAm Hamiltonian can be used in molecular calculations without further modifications. This is illustrated in Fig. 1 where the GSE of ZORA, IORA, and IORAm is plotted for the ground state of the U^{91+} ion as a function of the gauge shift Δ .

Expanding the one-electron wave functions (orbitals) ψ_i in terms of (nonorthogonal) basis set functions χ according to Eq. (8)

$$\psi_i = |\chi\rangle C_i, \quad (8)$$

where $|\chi\rangle$ is a row vector of basis functions and C_i is a column vector of expansion coefficients, the matrix form of the IORA (or IORAm) Hamiltonian is given by¹⁹

$$\mathbf{H} = \langle \chi | \hat{H} | \chi \rangle = (\mathbf{S}^{1/2})^\dagger (\mathbf{U}^{-1/2})^\dagger (\mathbf{V} + \mathbf{K}_1) (\mathbf{U}^{-1/2}) (\mathbf{S}^{1/2}), \quad (9)$$

where \mathbf{S} denotes the matrix of the overlap integrals $S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$ and \mathbf{K}_1 the matrix of the operator

$$(\sigma \cdot \mathbf{p}) \frac{c^2}{2mc^2 - V} (\sigma \cdot \mathbf{p}).$$

The matrix \mathbf{U} is given by

$$\mathbf{U} = \begin{cases} \mathbf{S} + \mathbf{K}_2 & \text{(IORA)} \\ \mathbf{S} + \frac{1}{4mc^2} \mathbf{K}_1 + \frac{1}{2} \mathbf{K}_2 & \text{(IORAm)}, \end{cases} \quad (10)$$

where \mathbf{K}_2 is the matrix of the operator

$$(\sigma \cdot \mathbf{p}) \frac{c^2}{(2mc^2 - V)^2} (\sigma \cdot \mathbf{p}).$$

The major obstacle in evaluating the elements of matrices \mathbf{K}_1 and \mathbf{K}_2 is the presence of the potential V in the denominator. Thus, in the case of a general potential V , an analytic expression for these matrix elements can hardly be derived in a closed form. However, representing the operator

$$\hat{K} = \frac{c^2}{2mc^2 - V} \quad (11)$$

as in Eq. (12),

$$\hat{K} = \frac{1}{2m} + \frac{1}{2mc^2} V \hat{K}, \quad (12)$$

and using the spectral RI, $\hat{I} = |\phi\rangle\langle\phi|$, in terms of the kinetically balanced^{24,25} basis set $|\phi\rangle$,

$$|\phi\rangle = |(\sigma \cdot \mathbf{p})\chi\rangle \frac{\mathbf{T}^{-1/2}}{(2m)^{1/2}}, \quad (13)$$

leads to the following equation for the matrix elements $(\mathbf{K}_1)_{\mu\nu}$:

$$\begin{aligned} (\mathbf{K}_1)_{\mu\nu} &= \left\langle (\sigma \cdot \mathbf{p})\chi_\mu \left| \frac{c^2}{2mc^2 - V} \right| (\sigma \cdot \mathbf{p})\chi_\nu \right\rangle \\ &= \mathbf{T}_{\mu\nu} + \frac{1}{2mc^2} \langle (\sigma \cdot \mathbf{p})\chi_\mu | V \times \hat{K} | (\sigma \cdot \mathbf{p})\chi_\nu \rangle \\ &= \mathbf{T}_{\mu\nu} + (\mathbf{W}_0 \mathbf{T}^{-1} \mathbf{K}_1)_{\mu\nu}, \end{aligned} \quad (14)$$

where \mathbf{T} is the matrix of the kinetic energy operator \hat{T} ,

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

and \mathbf{W}_0 is the matrix of the operator \hat{W}_0 ,

$$\hat{W}_0 = (\sigma \cdot \mathbf{p}) \frac{V}{4m^2 c^2} (\sigma \cdot \mathbf{p}).$$

Cross \times in the second line of Eq. (14) marks the place at which the RI is inserted. Representing \mathbf{K}_1 as

$$\mathbf{K}_1 = \mathbf{T} + \mathbf{W}, \quad (15)$$

Eq. (16) for matrix \mathbf{W} is obtained

$$\mathbf{W} = \mathbf{W}_0 + \mathbf{W}_0 \mathbf{T}^{-1} \mathbf{W} \quad (16)$$

with the solution

$$\mathbf{W}^{-1} = \mathbf{W}_0^{-1} - \mathbf{T}^{-1}. \quad (17)$$

Using the relationship

$$\begin{aligned} 2m\hat{K}^2 &= \frac{1}{2m} \frac{1}{(1 - (V/2mc^2))^2} \\ &= \frac{1}{2m} + \frac{1}{mc^2} V \hat{K} + 2m\hat{K} \frac{V}{2mc^2} \frac{V}{2mc^2} \hat{K} \end{aligned} \quad (18)$$

the elements of matrix \mathbf{K}_2 can be expressed as in Eq. (19),

TABLE I. Comparison of the nonrelativistic, IORA, and IORAm ground state energies (in hartree) of U^{91+} for different basis sets.

N^a	Nonrelativistic ^b	IORA ^c	ΔE^{IORAd}	IORAm	$\Delta E^{IORAm d}$
62 ^e	-4232.0000	-4921.0986	-689.0986	-4841.1766	-609.1766
28 ^f	-4231.9999	-4920.8645	-688.8646	-4841.0079	-609.0080
14 ^g	-4228.9538	-4914.5566	-685.6028	-4835.3816	-606.4278
7 ^g	-3639.8428	-4317.6384	-677.7956	-4256.8133	-616.9705

^aNumber of primitive Gaussian functions.

^bThe exact nonrelativistic value is -4232.0000 hartree. The exact Dirac value is -4861.1980 hartree.

^cThe exact IORA value is -4921.0993 hartree (Ref. 8).

^d $\Delta E^{\text{method}} = E^{\text{method}} - E^{\text{nonrel}}$.

^eBasis of 62 primitive Gaussian *s*-type functions from Ref. 15.

^fBasis of 28 primitive Gaussian *s*-type functions from Ref. 26.

^gObtained from the previous basis by excluding every second primitive function.

$$\begin{aligned}
 (\mathbf{K}_2)_{\mu\nu} &= \frac{1}{2mc^2} \langle (\boldsymbol{\sigma} \cdot \mathbf{p}) \chi_\mu | 2m \hat{K}^2 | (\boldsymbol{\sigma} \cdot \mathbf{p}) \chi_\nu \rangle \\
 &= \frac{1}{2mc^2} \left(\mathbf{T}_{\mu\nu} + 2 \left\langle (\boldsymbol{\sigma} \cdot \mathbf{p}) \chi_\mu \left| \frac{V}{2mc^2} \hat{K} \right| (\boldsymbol{\sigma} \cdot \mathbf{p}) \chi_\nu \right\rangle \right. \\
 &\quad \left. + 2m \left\langle (\boldsymbol{\sigma} \cdot \mathbf{p}) \chi_\mu \left| \hat{K} \frac{V}{2mc^2} \times \frac{V}{2mc^2} \hat{K} \right| \right. \right. \\
 &\quad \left. \left. \times (\boldsymbol{\sigma} \cdot \mathbf{p}) \chi_\nu \right\rangle \right) = \frac{1}{2mc^2} (\mathbf{T} + 2\mathbf{W} + \mathbf{W}\mathbf{T}^{-1}\mathbf{W}).
 \end{aligned} \tag{19}$$

Note that in the third line of Eq. (19) the RI formed with the auxiliary basis set (13) is used. Thus, the matrix elements of the IORA and IORAm Hamiltonian can easily be calculated¹⁹ with the use of Eqs. (9), (10), (14), (15), (17), and (19).

Although the present approach uses the RI, the quality of the results is not very sensitive to the size of the basis set employed. This is documented in Table I, where the IORA and IORAm energy calculated for the ground state of U^{91+} ion is presented as a function of the basis set size. Reducing more than twice the size of the basis set from 62 to 28 primitive functions does not result in a significant loss of accuracy. Even with the smallest basis set comprising only seven primitive functions the relativistic correction to the nonrelativistic energy is reproduced with a relative accuracy better than 2%.

While for the one-electron case the transformation of the relativistic Hamiltonian to the two-component form and the application of further approximations are straightforward,^{8,27,28} the transformation of the many-electron Hamiltonian is much more laborious due to the presence of two-electron terms. One should be content with certain approximations to simplify molecular calculations and the underlying theory. The use of a relativistically corrected one-electron Hamiltonian in many-electron equations represents an example of such an approximation.^{27,28} This one-electron ($1\bar{e}$) approximation is used in many quasirelativistic theories, e.g., in the Douglas–Kroll–Hess method,^{15,29} etc.^{27,30,31} As has been shown in Refs. 27 and 28, such an approximation corresponds to neglecting the commutators of the linear momentum operator ($\boldsymbol{\sigma} \cdot \mathbf{p}$) with the electron–electron repul-

sion operator $1/r_{ij}$. This implies neglecting a renormalized two-electron Darwin term which has the same order of magnitude as the two-electron spin–orbit term. Hence, the $1\bar{e}$ approximation should perform reasonably within the scalar-relativistic (one-component) approach where all spin-dependent relativistic effects are neglected.^{27,28}

Thus, the Hartree–Fock IORA (or IORAm) equations within the scalar-relativistic $1\bar{e}$ approximation read

$$\begin{aligned}
 &((\mathbf{S}^{1/2})^\dagger (\mathbf{U}^{-1/2})^\dagger (\mathbf{V}_n + \mathbf{T} + \mathbf{W}) (\mathbf{U}^{-1/2}) (\mathbf{S}^{1/2}) + \mathbf{J} - \mathbf{K}) \mathbf{C}_i \\
 &= \mathbf{S} \mathbf{C}_i \epsilon_i,
 \end{aligned} \tag{20}$$

where \mathbf{V}_n is the matrix of the electron–nuclear attraction integrals $\langle \chi_\mu | V_n | \chi_\nu \rangle$ and the matrix \mathbf{U} is given by

$$\mathbf{U} = \mathbf{S} + \frac{1}{2mc^2} (\mathbf{T} + a\mathbf{W} + b\mathbf{W}\mathbf{T}^{-1}\mathbf{W}) \tag{21}$$

with the parameters a and b for IORA: $a=2$, $b=1$ and for IORAm: $a=\frac{3}{2}$, $b=\frac{1}{2}$. The matrix \mathbf{W}_0 in Eq. (17) is calculated in the $1\bar{e}$ scalar-relativistic approximation as

$$\mathbf{W}_0 = \left\langle \chi_\mu \left| \mathbf{p} \frac{V_n}{4m^2c^2} \mathbf{p} \right| \chi_\nu \right\rangle. \tag{22}$$

Note that only the electron–nuclear attraction potential V_n is used in Eq. (22) and the electron–electron repulsion is treated nonrelativistically. The matrix \mathbf{W}_0 can be expressed¹⁹ in terms of the usual electron–nuclear attraction integrals, which are routinely available in the standard nonrelativistic quantum-chemical packages. The total SCF energy is given by

$$\begin{aligned}
 E_{\text{SCF}} &= \text{tr} \left(\frac{1}{2} \mathbf{P} (\mathbf{H} + \mathbf{F}) \right) \\
 &= \text{tr} \left(\mathbf{P} \left((\mathbf{S}^{1/2})^\dagger (\mathbf{U}^{-1/2})^\dagger \right. \right. \\
 &\quad \left. \left. \times (\mathbf{V}_n + \mathbf{T} + \mathbf{W}) (\mathbf{U}^{-1/2}) (\mathbf{S}^{1/2}) + \frac{1}{2} (\mathbf{J} - \mathbf{K}) \right) \right),
 \end{aligned} \tag{23}$$

where \mathbf{P} is the density matrix in the basis of atomic orbitals χ ,

$$\mathbf{P} = \mathbf{C} \mathbf{n} \mathbf{C}^\dagger. \tag{24}$$

In Eq. (24), \mathbf{n} is the diagonal matrix of orbital occupation numbers.

Equation (23) differs from the corresponding nonrelativistic expression only in the use of the relativistically corrected one-electron Hamiltonian $\mathbf{H}_{1\bar{e}}$ in the one-electron contribution to the total SCF energy, Eq. (25),

$$E_{1\bar{e}} = \text{tr}(\mathbf{P}\mathbf{H}_{1\bar{e}}) = \text{tr}(\mathbf{P}((\mathbf{S}^{1/2})^\dagger(\mathbf{U}^{-1/2})^\dagger(\mathbf{V}_n + \mathbf{T} + \mathbf{W}) \times (\mathbf{U}^{-1/2})(\mathbf{S}^{1/2}))). \quad (25)$$

Let us assume that the molecular integrals in Eqs. (23) and (25) depend on an external parameter λ , e.g., nuclear coordinate. Then, the first derivative of the SCF total energy with respect to the parameter λ is given in³²

$$\begin{aligned} \frac{\partial E}{\partial \lambda} &= \text{tr}\left(\mathbf{P}\left(\frac{\partial}{\partial \lambda}\mathbf{H}\right)\right) + \text{tr}\left(\mathcal{W}\left(\frac{\partial}{\partial \lambda}\mathbf{S}\right)\right) \\ &+ \frac{1}{2}\text{tr}\left(\mathbf{P}'\left(\frac{\partial}{\partial \lambda}(\mathbf{J} - \mathbf{K})\right)\right), \end{aligned} \quad (26)$$

where \mathcal{W} is the energy-weighted density matrix,

$$\mathcal{W} = \mathbf{C}\mathbf{n}\epsilon\mathbf{C}^\dagger, \quad (27)$$

ϵ is a diagonal matrix of orbital energies, and 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.

The IORA (or IORAm) one-electron contribution to the derivative of the total energy is given as follows:

$$\begin{aligned} \frac{\partial E_{1\bar{e}}}{\partial \lambda} &= \text{tr}\left(\mathbf{P}\left(\frac{\partial}{\partial \lambda}((\mathbf{S}^{1/2})^\dagger(\mathbf{U}^{-1/2})^\dagger(\mathbf{V}_n + \mathbf{T} + \mathbf{W})(\mathbf{U}^{-1/2}) \times (\mathbf{S}^{1/2}))\right)\right) \\ &= \text{tr}\left(\mathbf{P}\left(\left(\frac{\partial}{\partial \lambda}\mathbf{G}^\dagger\right)\mathbf{H}\mathbf{G} + \mathbf{G}^\dagger\left(\frac{\partial}{\partial \lambda}\mathbf{H}\right)\mathbf{G} + \mathbf{G}^\dagger\mathbf{H}\left(\frac{\partial}{\partial \lambda}\mathbf{G}\right)\right)\right) \\ &= \text{tr}\left(\left(\mathbf{G}\mathbf{P}\left(\frac{\partial}{\partial \lambda}\mathbf{G}^\dagger\right) + \left(\frac{\partial}{\partial \lambda}\mathbf{G}\right)\mathbf{P}\mathbf{G}^\dagger\right)\mathbf{H}\right) \\ &+ \text{tr}\left(\left(\mathbf{G}\mathbf{P}\mathbf{G}^\dagger\right)\left(\frac{\partial}{\partial \lambda}\mathbf{H}\right)\right) \\ &= \text{tr}\left(\left(\frac{\partial'}{\partial \lambda}\mathbf{P}'\right)\mathbf{H}\right) + \text{tr}\left(\mathbf{P}'\left(\frac{\partial}{\partial \lambda}\mathbf{H}\right)\right), \end{aligned} \quad (28)$$

where the matrices \mathbf{G} , \mathbf{H} , and \mathbf{P}' are defined in Eqs. (29), (30), and (31), respectively,

$$\mathbf{G} = \mathbf{U}^{-1/2}\mathbf{S}^{1/2}, \quad (29)$$

$$\mathbf{H} = \mathbf{V}_n + \mathbf{T} + \mathbf{W}, \quad (30)$$

$$\mathbf{P}' = \mathbf{G}\mathbf{P}\mathbf{G}^\dagger. \quad (31)$$

The derivative of the \mathbf{H} matrix,

$$\frac{\partial}{\partial \lambda}\mathbf{H} = \frac{\partial}{\partial \lambda}\mathbf{V}_n + \frac{\partial}{\partial \lambda}\mathbf{T} + \frac{\partial}{\partial \lambda}\mathbf{W}, \quad (32)$$

contains the derivatives of the electron–nuclear attraction $((\partial/\partial\lambda)\mathbf{V}_n)$ and the kinetic energy integrals $((\partial/\partial\lambda)\mathbf{T})$, which are easily available in standard quantum-chemical codes, as well as the derivative of matrix \mathbf{W} defined in Eq. (16). The latter derivative can be obtained from differentiating the identity $\mathbf{A}^{-1}\mathbf{A} = \mathbf{I}$ as in the following:

$$\frac{\partial}{\partial \lambda}\mathbf{A}^{-1} = -\mathbf{A}^{-1}\left(\frac{\partial}{\partial \lambda}\mathbf{A}\right)\mathbf{A}^{-1}, \quad (33)$$

which for the derivative of the \mathbf{W} matrix yields

$$\begin{aligned} \frac{\partial}{\partial \lambda}\mathbf{W} &= -\mathbf{W}\left(\frac{\partial}{\partial \lambda}(\mathbf{W}_0^{-1} - \mathbf{T}^{-1})\right)\mathbf{W} \\ &= \mathbf{W}\mathbf{W}_0^{-1}\left(\frac{\partial}{\partial \lambda}\mathbf{W}_0\right)\mathbf{W}_0^{-1}\mathbf{W} \\ &- \mathbf{W}\mathbf{T}^{-1}\left(\frac{\partial}{\partial \lambda}\mathbf{T}\right)\mathbf{T}^{-1}\mathbf{W}. \end{aligned} \quad (34)$$

Thus, the derivative of the \mathbf{H} matrix with respect to a parameter λ as given in Eq. (35) can be expressed in terms of the usual molecular integrals accessible in standard nonrelativistic quantum-chemical packages,

$$\begin{aligned} \frac{\partial}{\partial \lambda}\mathbf{H} &= \frac{\partial}{\partial \lambda}\mathbf{V}_n + \frac{\partial}{\partial \lambda}\mathbf{T} + \mathbf{W}\mathbf{W}_0^{-1}\left(\frac{\partial}{\partial \lambda}\mathbf{W}_0\right)\mathbf{W}_0^{-1}\mathbf{W} \\ &- \mathbf{W}\mathbf{T}^{-1}\left(\frac{\partial}{\partial \lambda}\mathbf{T}\right)\mathbf{T}^{-1}\mathbf{W}. \end{aligned} \quad (35)$$

The derivative of the renormalization matrix \mathbf{G} with respect to parameter λ is given as follows:

$$\begin{aligned} \frac{\partial}{\partial \lambda}\mathbf{G} &= \frac{\partial}{\partial \lambda}(\mathbf{U}^{-1/2}\mathbf{S}^{1/2}) \\ &= \left(\frac{\partial}{\partial \lambda}\mathbf{U}^{-1/2}\right)\mathbf{S}^{1/2} + \mathbf{U}^{-1/2}\left(\frac{\partial}{\partial \lambda}\mathbf{S}^{1/2}\right) \\ &= -\mathbf{U}^{-1/2}\left(\frac{\partial}{\partial \lambda}\mathbf{U}^{1/2}\right)\mathbf{G} + \mathbf{U}^{-1/2}\left(\frac{\partial}{\partial \lambda}\mathbf{S}^{1/2}\right), \end{aligned} \quad (36)$$

which contains the derivatives of the $\mathbf{U}^{1/2}$ and $\mathbf{S}^{1/2}$ matrices. The latter derivatives can be taken³³ using the properties of eigenvalues and eigenvectors of a symmetric matrix \mathbf{A} which can be diagonalized with the help of its eigenvectors \mathbf{C} as in the following:

$$\mathbf{a} = \mathbf{C}^\dagger\mathbf{A}\mathbf{C}. \quad (37)$$

Differentiating the diagonal matrix \mathbf{a} one obtains

$$\frac{\partial}{\partial \lambda}\mathbf{a} = \left(\frac{\partial}{\partial \lambda}\mathbf{C}^\dagger\right)\mathbf{A}\mathbf{C} + \mathbf{C}^\dagger\left(\frac{\partial}{\partial \lambda}\mathbf{A}\right)\mathbf{C} + \mathbf{C}^\dagger\mathbf{A}\left(\frac{\partial}{\partial \lambda}\mathbf{C}\right). \quad (38)$$

Differentiating the identity $\mathbf{C}\mathbf{C}^\dagger = \mathbf{I}$, it can be established that $\mathbf{R} = \mathbf{C}^\dagger((\partial/\partial\lambda)\mathbf{C})$ is an antisymmetric matrix. Using the antisymmetry of \mathbf{R} and the identity $\mathbf{A} = \mathbf{C}\mathbf{a}\mathbf{C}^\dagger$, Eq. (38) can be transformed to

$$\frac{\partial}{\partial \lambda}\mathbf{a} = \mathbf{a}\mathbf{R} - \mathbf{R}\mathbf{a} + \mathbf{C}^\dagger\left(\frac{\partial}{\partial \lambda}\mathbf{A}\right)\mathbf{C}. \quad (39)$$

Noting that the matrix \mathbf{a} is diagonal and the antisymmetric matrix \mathbf{R} has vanishing diagonal elements, Eq. (40) is obtained for the elements of the \mathbf{R} matrix,

$$\mathbf{R}_{ij} = \begin{cases} (\mathbf{a}_{jj} - \mathbf{a}_{ii})^{-1} \left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \lambda} \mathbf{A} \right) \mathcal{C} \right)_{ij}, & i \neq j \\ 0, & i = j. \end{cases} \quad (40)$$

Analogously, for the square root of a diagonal matrix \mathbf{a} one has

$$\frac{\partial}{\partial \lambda} \mathbf{a}^{1/2} = \mathbf{a}^{1/2} \mathbf{R} - \mathbf{R} \mathbf{a}^{1/2} + \mathcal{C}^\dagger \left(\frac{\partial}{\partial \lambda} \mathbf{A}^{1/2} \right) \mathcal{C}, \quad (41)$$

which after substituting Eq. (40) and noting that for the derivative of a diagonal element of the matrix $\mathbf{a}^{1/2}$ the following holds:

$$\frac{\partial}{\partial \lambda} \mathbf{a}_{ii}^{1/2} = \frac{1}{2} \mathbf{a}_{ii}^{-1/2} \frac{\partial}{\partial \lambda} \mathbf{a}_{ii} = \frac{1}{2} \mathbf{a}_{ii}^{-1/2} \left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \lambda} \mathbf{A} \right) \mathcal{C} \right)_{ii} \quad (42)$$

and yields Eq. (43) for the derivative of the square root matrix $\mathbf{A}^{1/2}$,

$$\begin{aligned} \left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \lambda} \mathbf{A}^{1/2} \right) \mathcal{C} \right)_{ij} &= (\mathbf{a}_{jj}^{1/2} - \mathbf{a}_{ii}^{1/2}) \mathbf{R}_{ij} \\ &= (\mathbf{a}_{jj}^{1/2} + \mathbf{a}_{ii}^{1/2})^{-1} \left(\mathcal{C}^\dagger \left(\frac{\partial}{\partial \lambda} \mathbf{A} \right) \mathcal{C} \right)_{ij}. \end{aligned} \quad (43)$$

The derivatives of matrices $\mathbf{U}^{1/2}$ and $\mathbf{S}^{1/2}$ can be calculated utilizing Eq. (43). The derivatives of the overlap integrals which are necessary to calculate $(\partial/\partial\lambda)\mathbf{S}^{1/2}$ are available in standard quantum-chemical programs while the derivatives of matrix \mathbf{U} are expressed in Eq. (44) in terms of the usual one-electron molecular integrals,

$$\begin{aligned} \frac{\partial}{\partial \lambda} \mathbf{U} &= \frac{\partial}{\partial \lambda} \mathbf{S} + \frac{1}{2mc^2} \left(\frac{\partial}{\partial \lambda} \mathbf{T} - (a+b) \mathbf{W} \mathbf{T}^{-1} \left(\frac{\partial}{\partial \lambda} \mathbf{T} \right) \mathbf{T}^{-1} \mathbf{W} - b \right. \\ &\quad \times \left(\mathbf{W} \mathbf{T}^{-1} \left(\frac{\partial}{\partial \lambda} \mathbf{T} \right) \mathbf{T}^{-1} \mathbf{W} \mathbf{T}^{-1} \mathbf{W} + \mathbf{W} \mathbf{T}^{-1} \mathbf{W} \mathbf{T}^{-1} \left(\frac{\partial}{\partial \lambda} \mathbf{T} \right) \mathbf{T}^{-1} \mathbf{W} \right) + a \mathbf{W} \mathbf{W}_0^{-1} \left(\frac{\partial}{\partial \lambda} \mathbf{W}_0 \right) \mathbf{W}_0^{-1} \mathbf{W} + b \\ &\quad \left. \times \left(\mathbf{W} \mathbf{W}_0^{-1} \left(\frac{\partial}{\partial \lambda} \mathbf{W}_0 \right) \mathbf{W}_0^{-1} \mathbf{W} \mathbf{T}^{-1} \mathbf{W} + \mathbf{W} \mathbf{T}^{-1} \mathbf{W} \mathbf{W}_0^{-1} \left(\frac{\partial}{\partial \lambda} \mathbf{W}_0 \right) \mathbf{W}_0^{-1} \mathbf{W} \right) \right). \end{aligned} \quad (44)$$

Thus, the implementation of the IORA and IORAm methods in the one-electron scalar-relativistic approximation does not require the calculation of any unusual molecular integrals and can easily be achieved within standard nonrelativistic quantum-chemical codes. Because only one-electron part of the total energy is modified, the formalism presented is applicable at various correlation corrected levels of theory as well.

III. IMPLEMENTATION AND DETAILS OF CALCULATIONS

Implementation of analytical energy derivatives. The computational scheme described in Sec. II was programmed and implemented into the COLOGNE 2002³⁴ suite of quantum-chemical programs. Analytical derivatives were tested with the help of numerical derivatives whereas the latter were evaluated from a one-dimensional mesh with the step length of 0.005 Å.

For the three gold-containing diatomic molecules AuH, AuF, and Au₂, numeric (computed with the central difference formula) and analytic energy derivatives determined at points close to the equilibrium bond length are compared in Table II. The discrepancy between numeric and analytic derivatives calculated at the IORA/SCF, IORAm/SCF, IORA/MP2, and IORAm/MP2 levels of theory (for the basis set used, see the following) varies between 10⁻⁵ and

10⁻⁶ hartree/bohr, which is far less than a convergence criterion of ~10⁻⁴ hartree/bohr used for geometry optimizations in standard quantum-chemical programs. A reduction of the increment length of 0.005 Å leads to an even better agreement between numeric and analytic derivatives.

A second test was carried out by comparing the results of

TABLE II. Analytic vs numeric energy derivatives (in hartree/bohr) of Au-containing diatomic molecules.

Method	R_{AB} (Å) ^a	Analytic derivative	Numeric derivative
AuH			
IORA/SCF	1.545	-0.002 823	-0.002 831
IORAm/SCF	1.555	-0.003 768	-0.003 773
IORA/MP2	1.465	-0.005 330	-0.005 345
IORAm/MP2	1.475	-0.005 093	-0.005 103
AuF			
IORA/SCF	1.905	-0.005 715	-0.005 726
IORAm/SCF	1.965	-0.003 819	-0.003 826
IORA/MP2	1.845	-0.006 035	-0.006 053
IORAm/MP2	1.895	-0.005 363	-0.005 377
Au₂			
IORA/SCF	2.060	-0.012 978	-0.013 007
IORAm/SCF	2.565	-0.002 389	-0.002 392
IORA/MP2	2.005	-0.015 627	-0.015 657
IORAm/MP2	2.420	-0.003 688	-0.003 679

^aInteratomic distance at which the derivative is calculated.

TABLE III. Equilibrium bond lengths (in Å) of Au-containing diatomic molecules optimized numerically and with the use of analytic energy derivatives.

Method	Analytic optimization	Numeric optimization
AuH^a		
IORA/SCF	1.5532	1.5531
IORAmm/SCF	1.5671	1.5663
IORA/MP2	1.4757	1.4757
IORAmm/MP2	1.4857	1.4857
AuF^b		
IORA/SCF	1.9176	1.9176
IORAmm/SCF	1.9751	1.9756
IORA/MP2	1.8560	1.8560
IORAmm/MP2	1.9071	1.9071
Au₂		
IORA/SCF	2.0700	2.0700
IORAmm/SCF	2.5768	2.5768
IORA/MP2	2.0154	2.0151
IORAmm/MP2	2.4321	2.4321

^aInteratomic distance from DHF: 1.570 Å; from DHF/MP2: 1.485 Å (Ref. 40).

^bInteratomic distance from DHF: 1.968 Å; from DHF/MP2: 1.899 Å (Ref. 41).

a numeric bond length optimization with that of an optimization based on the analytic energy derivatives developed and programmed in this work (see Table III). Numerically and analytically calculated bond lengths differ by less than 10^{-3} Å, most of them by less than 10^{-4} Å, whereas the latter difference is given by the convergence criterion in the geometry optimization.

A comparison of the computer times for the SCF part and the gradient part revealed that the additional work needed for setting up the analytic energy gradient requires not more than 20% of the SCF calculation of an IORA/SCF, IORAmm/SCF, IORA/MP2, or IORAmm/MP2 approach (with 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 IORA and IORAmm methods reduces the time needed for the total geometry optimization substantially and leads to accurate geometries.

Computational details. A block-contracted [14s10p9d3f] basis set for gold was constructed from the basis set of Gropen³⁵ using prescriptions outlined in Ref. 36. The original basis set was partially decontracted. Three innermost and six outermost primitive Gaussian functions of *s*-type and three outermost primitive functions of *p*-type were decontracted. The remaining ten *s*-orbitals were contracted in a pattern 3/3/2/2 using the contraction coefficients for 1*s*, 2*s*, 3*s*, and 4*s* orbitals. For the ten *p* orbitals the contraction pattern 4/3/3 was applied employing the contraction coefficients for 2*p*, 3*p*, and 4*p* orbitals. The outermost primitive *d*-type function was dropped due to orthogonality problems and the next four outermost orbitals were decontracted. The remaining five *d* orbitals were contracted in a 3/2 pattern using the contraction coefficients for the 3*d* orbital. One outermost *f*-type primitive function was decontracted. The so-obtained block-contracted basis set was aug-

mented with one diffuse *s* and one *f* function and three diffuse *p* and three *d* functions in a well-tempered sequence based on the ratio of 2.5.

In the calculations on xenone hexafluoride, the block-contracted [12s9p6d2f] basis set for xenone was used. The basis set was derived from the spin-free relativistic basis set of Dyall.³⁷ The innermost *s*-type and *p*-type primitive function and the outermost five *s*-type, three *p*-type, and three *d*-type primitive functions were decontracted. The remaining thirteen *s*-type functions were block-contracted in a 4/3/2/2/2 pattern employing the contraction coefficients for 1*s*, 2*s*, 3*s*, 4*s*, and 5*s* orbitals. Eleven *p*-type primitive functions remaining after decontraction were contracted in a 4/3/2/2 pattern using the contraction coefficients for 2*p*, 3*p*, 4*p*, and 5*p* orbitals. Six *d*-type orbitals were block-contracted in a 4/2 pattern using the coefficients for 3*d* and 4*d* orbitals. The basis set obtained in this way was augmented with a set of correlating functions including one *s*-, one *p*-, one *d*-, and one *f*-type primitive function and with one polarizing *f*-type primitive function.³⁷

For light elements, the correlation consistent augmented double-zeta basis set of Dunning,³⁸ aug-cc-pVDZ, was used. In the MP calculations on gold diatomics, all valence electrons of the light atom as well as 33 electrons of the gold atom (i.e., 5*s*, 4*f*, 5*p*, 5*d* and 6*s* electrons) were correlated. In the MP calculations of XeF₆, 4*d*, 5*s* and 5*p* electrons of xenone atom were correlated together with 2*s* and 2*p* electrons of the fluorine atoms.

IV. RESULTS AND DISCUSSION

The three gold containing diatomics AuH, AuF, and Au₂ were investigated in this work for three reasons. First, they represent suitable benchmarks for assessing the accuracy of the computational formalism described (see Sec. III). Second, their choice was motivated by the importance of relativistic effects for chemical bonding in gold compounds.³⁹ Finally, for some of these molecules (AuH and AuF) the results of Dirac–Hartree–Fock (DHF) and post-DHF calculations are available,^{40,41} which enables one to make a comparison with results obtained from the exact (four-component) computational approach and to assess thereby the quality of the approximate schemes.

The bond lengths optimized with IORAmm (SCF and MP2) compare well with available DHF and DHF/MP2 results,^{40,41} whereas the bond lengths produced by IORA are generally too short (see Table III). This is a consequence of the gauge noninvariance of the IORA total energy.^{8,11,12} In molecules, tails of the nuclear potentials of neighboring atoms play the role of a constant gauge shift for the core electrons on a given atom. Since the IORA orbital energies decrease by an amount slightly larger than the gauge shift value, an attractive extra force between the nuclei emerges. While for AuH the extra force results in a modest distortion of the molecular structure (compared to DHF and DHF/MP2),^{40,41} for diatomics with heavier elements the distortion is substantial.

For Au₂ the bond length optimized with IORA is almost half of an ångstrom shorter than the experimental value of 2.472 Å.⁴² At the same time, the IORAmm/MP2 method

TABLE IV. Spectroscopic parameters of gold diatomic molecules calculated with IORAmM/MP4(SDQ) method.

Molecule	Method	R_e (Å)	ω_e (cm ⁻¹)	D_e (eV)
AuH	Calc	1.510	2400	3.20
	Expt ^a	1.524	2305	3.36
AuF	Calc	1.927	570	3.00
	Expt	1.918 ^b	560 ^c	3.20 ^d
Au ₂	Calc	2.477	190	2.23
	Expt	2.472	191	2.29

^aExperimental data taken from Ref. 42 unless noted otherwise.

^bTaken from Ref. 44.

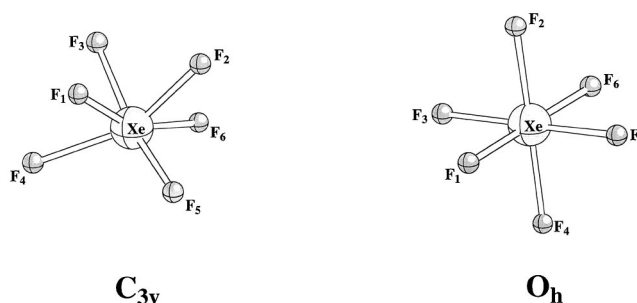
^cTaken from Ref. 45.

^dTaken from Ref. 46.

yields for Au₂ the bond length 2.432 Å, which is in reasonable agreement with the experimental value of 2.472 Å⁴² (Table III) and those obtained with other quasirelativistic methods. For example, an MP2 calculation with the Douglas–Kroll–Hess (DKH) one-electron Hamiltonian, which correlated 34 electrons and employed a [13s11p6d4f2g1h1i] basis set, yielded 2.418 Å for the Au–Au bond length.⁴³

Thus, the effect of the residual GSE in IORAmM does not show up during the geometry optimization and the method can be used without further modifications. However, calculating dissociation energies requires that the GSE is taken into account. This can be done¹⁹ in the atomic SCF calculation by taking the difference between the total atomic SCF energy E_0 calculated without gauge shift in the nuclear potential and the energy E_Δ calculated with the gauge shift Δ , $E_{\text{GSE}} = E_0 - E_\Delta + \Delta$. The latter calculation employs the wave function from the former one and does not optimize it. The value of the gauge shift Δ for a given atom A is calculated as a sum of values of the potentials of other nuclei in the molecule at the position of the atom A , $\Delta = \sum_{B \neq A} 1/R_{AB}$. The GSE for the IORAmM total energy depends nearly linearly on Δ (see Fig. 1) and, even for heavy atoms, it does normally not account for more than a few kilocalories per mole.¹⁹ For light atoms (up to the third row elements) GSE is less than 0.1 kcal/mol and can safely be neglected.

Table IV summarizes the results of the IORAmM/MP4(SDQ) calculations of the spectroscopic constants of gold diatomics. When calculating the dissociation energies, the effect of the GSE was taken into account for the gold atom only. The GSE for Au in AuH, AuF, and Au₂ corresponds to 0.000 144 4, 0.001 047, and 0.008 464 2 hartree, respectively. Generally, the agreement between the calculated and the experimental spectroscopic constants is excellent. Especially gratifying is that even for the gold dimer the molecular structure and the vibrational frequency are not affected by the residual gauge noninvariance of the IORAmM Hamiltonian. The results for Au₂ from Table IV can be compared with the results of the DKH/MP4 calculations,⁴³ which yielded 2.442 Å for the bond length and 202 cm⁻¹ for the vibrational frequency. Note, however that the latter calculation employed the somewhat larger [13s11p6d4f2g1h1i] basis set and correlated fewer electrons, 34 in DKH/MP4

FIG. 2. Atom labels for the two conformers of XeF₆.

instead of 66 in the IORAmM/MP4(SDQ) calculation.

Turning to polyatomic molecules, the IORAmM calculations at the SCF, MP2, MP3, and MP4(SDQ) levels were carried out for XeF₆. Since its experimental discovery⁴⁷ the electronic structure of xenone hexafluoride has received extensive attention.^{48,49} As has been stressed by Kaupp *et al.*,⁴⁹ the relative stability of the two conformers of XeF₆ shown in Fig. 2 is governed by a delicate balance of relativistic effects and electronic correlation. While at the SCF level, the C_{3v} structure is most stable both in relativistic and nonrelativistic calculations, inclusion of electron correlation at the MP2 level stabilizes the O_h structure which will become the lowest energy structure if relativity is taken into account.^{48,49} This is in apparent contradiction with experiment, which established that the trigonally distorted octahedron should be more stable.^{47,50}

The results of the IORAmM calculations for the two conformers of XeF₆ are summarized in Table V. The reported total molecular energies are corrected for the GSE in the same way as it has been done for gold containing molecules. The trigonally distorted octahedron is the most stable structure at the SCF, MP3, and MP4(SDQ) levels of theory while at the MP2 level the regular octahedron is favored. Indeed, as has been pointed out in earlier work on XeF₆ (Ref. 49), MP2 overestimates correlation effects (for a general discussion, see Ref. 51). Generally,⁵¹ MP3 tend to overcorrect the MP2 error while MP4 shifts the correlation energy back into the direction of the MP2 result. Because the convergence of the MP_n series is nonmonotonous,⁵¹ the correct energy may lie somewhere in between the MP3 and MP4 values. Thus, it may be expected that the energy difference between the regular and trigonally distorted octahedral structures is bracketed by the MP3 value of 7.0 (from above) and the MP4 value 1.4 kcal/mol (from below). Note that for both MP3 and MP4 the optimized molecular geometry of the C_{3v} conformer is in reasonably good agreement with the available experimental data (see Table V).⁵⁰ Almost all structural parameters fall within the error bars of the experimental measurement.

V. CONCLUSIONS

A compact and reliable representation for the matrix elements of the quasirelativistic Hamiltonian within the regular approximation is presented. Despite the fact that the new computational procedure uses the spectral RI technique, no additional molecular integrals, which involve an auxiliary

TABLE V. Structural parameters (in Å) for XeF₆ calculated with IORamm.

Parameter	Expt ^a	SCF	MP2	MP3	MP4(SDQ)
		C_{3v}			
Xe-F ₁	1.850±0.036	1.767	n.a. ^b	1.818	1.838
Xe-F ₂	1.941±0.036	1.920	n.a.	1.942	1.958
F ₁ -F ₂	2.535±0.208	2.284	n.a.	2.354	2.394
F ₄ -F ₅	3.106±0.302	3.223	n.a.	3.228	3.217
F ₁ -F ₅	2.498±0.108	2.338	n.a.	2.420	2.479
F ₁ -F ₆	3.757±0.070	3.582	n.a.	3.668	3.721
E_{tot}^c		-8037.314867	n.a.	-8039.190 543	-8039.242 876
		O_h			
Xe-F ₁	...	1.888	1.938	1.913	1.930
E_{tot}		-8037.267 944	-8039.314 422	-8039.179 452	-8039.240 648
ΔE^d		29.4	...	7.0	1.4

^aTaken from Ref. 50.^bOptimization converges to O_h structure.^cTotal molecular energy (in hartree) corrected for GSE.^d $\Delta E = E_{\text{tot}}(O_h) - E_{\text{tot}}(C_{3v})$ (in kcal/mol).

basis set used to resolve the identity operator, appear in the final formulas for the Hamiltonian matrix elements. This makes an implementation of new technique within the standard nonrelativistic quantum-chemical programs straightforward and easy.

A modification to the IORA⁸ is described, which reduces considerably the erroneous gauge dependence of the IORA total energy. The IORamm (IORA with modified metric) method¹⁹ can be used in molecular calculations without further modifications designed to reduce the gauge dependence of the energy.^{6,7,18}

The analytic expressions for the derivatives of the total molecular energy with respect to external parameters (nuclear coordinates, external electric fields, etc.) are derived and presented in matrix form suitable for implementation in the standard quantum-chemical codes. The formalism developed is tested in *ab initio* calculations on a number of compounds containing heavy elements. The benchmark calculations demonstrate the following.

(i) The IORamm/SCF and IORamm/MP2 results for gold containing diatomic molecules are in reasonable agreement with the results obtained by the exact four-component formalism.^{40,41} At the same time the IORA method suffers from the gauge dependence problem which results in a marked distortion of the molecular geometry.

(ii) The IORamm method in combination with correlation corrected *ab initio* approaches exhibits high precision in describing the electronic and molecular structure of compounds containing heavy elements. The experimental structural and energetic data^{42,44-46} for gold diatomic molecules are at least as accurate as the results of the corresponding nonrelativistic calculations for molecules containing light elements only.⁵¹ The molecular structure of xenone hexafluoride optimized with the IORamm/MP3 and IORamm/MP4(SDQ) methods is in good agreement with experimental measurements⁵⁰ and the correct minimal energy structure (trigonally distorted octahedron) is obtained.

Thus, the formalism presented enables one to obtain for compounds of heavy elements results of high quality as es-

entially the same price as that of conventional non-relativistic calculations.

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