



On representation of the Hamiltonian matrix elements in relativistic regular approximation

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Abstract

With the help of resolution of the identity (RI) a compact representation for the zeroth-order (ZORA) and infinite-order (IORA) regular approximation Hamiltonians in matrix form is developed. The new representation does not require calculation of any additional molecular integrals, which involve an auxiliary basis set used in the RI. The IORA computational scheme is modified in such a way that the erroneous gauge dependence of the total energy is reduced by an order of magnitude. The new quasi-relativistic method, dubbed IORamm, is tested along with the ZORA and IORA methods in atomic and molecular calculations performed at the SCF and MP2 level.

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1. Introduction

Development of relativistic Hamiltonians for electronic structure calculations is currently an active field of research in quantum chemistry. Computational complexity of four-component relativistic calculations which employ directly the Dirac Hamiltonian prompts researchers to seek for approximate two- or even one-component theories. Among such quasi-relativistic theories methods based on the regular approximation [1,2] are widely used. The zeroth-order and infinite-order regular approximations (ZORA and IORA, respectively) provide two-/one-component variationally stable Hamiltonian, which is used for

inclusion of relativistic effects into atomic and molecular calculations [3–9].

However, an implementation of ZORA and IORA in the standard quantum chemical codes is difficult, because the regular Hamiltonian contains the total atomic (or molecular) potential in the denominator. This complicates greatly the calculation of matrix elements of the ZORA and IORA Hamiltonians and makes the use of either numeric integration techniques or resolution of the identity (RI) inevitable. Within ab initio framework RI has been used in a series of works by Faas et al. [6–8] and Klopper et al. [9]. Although their results are in reasonable agreement with the numeric ZORA results, a relatively large auxiliary basis set is necessary to provide a good accuracy in the RI. Thus, such ab initio calculations are still much more costly than the non-relativistic calculations. Furthermore,

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the approach of [6–9] has not been tested in the post Hartree–Fock ab initio calculations.

Yet another disadvantage of the ZORA and IORA methods is an incorrect dependence of energy eigenvalues on the choice of gauge in the electrostatic potential [3–5,8,9]. This means that shifting the electrostatic potential by a certain amount does not result in exactly the same shift (as it should be) in eigenenergies. In molecular calculations such a gauge non-invariance results in an incorrect dependence of the ZORA energy on molecular structure [4]. Systematic reduction of the incorrect gauge dependence can be achieved with the use of a perturbation expansion [5], but perturbational methods are far less efficient than variational in calculation of properties other than energy. Within the quasi-variational approach the incorrect gauge dependence of ZORA energies is reduced greatly with the use of a quasi-relativistic metric [5,9]. Thus, employing in the IORA method [5] a wavefunction metric obtained from the regular expansion of the exact Foldy–Wouthuysen transformation [10] reduces the non-invariance error from order $1/c^2$ to order $1/c^4$ [5,9]. However, for heavy nuclei ($Z \geq 50$) the error is still large and can affect optimized molecular structures as well as calculated relative energies [9].

In the present Letter we propose a matrix representation for the ZORA (and IORA) Hamiltonian alternative to that used in [6–9]. The new representation is also based on RI, however the direct use of an auxiliary basis set is avoided in final formulae for the Hamiltonian matrix elements. Based on the IORA one-electron equations, an approximate quasi-relativistic scheme is proposed, which reduces considerably the gauge error in the IORA energies. The scheme dubbed IORAm (IORA with modified metric) was tested in the calculation of electronic structure of several atomic and molecular systems both at the SCF and post-SCF (MP2) level.

2. Theory

The one-electron ZORA equation is given by [3]

$$\left(\frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{1}{1 - \frac{V}{2mc^2}} (\boldsymbol{\sigma} \cdot \mathbf{p}) + V \right) \psi = \epsilon \psi, \quad (1)$$

where ψ is the ZORA wavefunction, V the potential, $\boldsymbol{\sigma}$ is vector of the Pauli matrices $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ [11], $\mathbf{p} = -i\hbar\nabla$ the momentum operator, c the velocity of light, and m is the electron mass. The IORA one-electron equation [5] differs from Eq. (1) in the use of quasi-relativistic metric on the right hand side (RHS) of Eq. (2).

$$\begin{aligned} & \left(\frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{1}{1 - \frac{V}{2mc^2}} (\boldsymbol{\sigma} \cdot \mathbf{p}) + V \right) \psi \\ & = \epsilon \left(1 + \frac{1}{4m^2 c^2} (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{1}{(1 - \frac{V}{2mc^2})^2} (\boldsymbol{\sigma} \cdot \mathbf{p}) \right) \psi. \end{aligned} \quad (2)$$

Expanding the wavefunction ψ in terms of (non-orthogonal) basis set $\boldsymbol{\chi}$ as in Eq. (3)

$$\psi = \boldsymbol{\chi} \mathbf{C}, \quad (3)$$

where $\boldsymbol{\chi}$ is a row-vector of basis functions and \mathbf{C} is a column-vector of expansion coefficients, Eqs. (1) and (2) can be represented in matrix form, Eqs. (4) and (5), respectively.

$$(\mathbf{V} + \mathbf{K}_1) \mathbf{C} = \mathbf{S} \mathbf{C} \epsilon, \quad (4)$$

$$(\mathbf{V} + \mathbf{K}_1) \mathbf{C} = (\mathbf{S} + \mathbf{K}_2) \mathbf{C} \epsilon. \quad (5)$$

In Eqs. (4) and (5) \mathbf{V} is the potential energy matrix, \mathbf{S} is the overlap matrix and \mathbf{K}_1 and \mathbf{K}_2 are the matrices of the operators

$$\frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{1}{1 - \frac{V}{2mc^2}} (\boldsymbol{\sigma} \cdot \mathbf{p})$$

and

$$\frac{1}{4m^2 c^2} (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{1}{(1 - \frac{V}{2mc^2})^2} (\boldsymbol{\sigma} \cdot \mathbf{p}),$$

respectively. Since, the elements of the \mathbf{K}_1 and \mathbf{K}_2 matrices contain V in the denominator, an analytic expression for calculating these elements can hardly be derived in the case of general potential V .

2.1. Resolution of the identity (RI)

First let us denote

$$K = \frac{1}{2m} \frac{1}{1 - \frac{V}{2mc^2}}. \quad (6)$$

The operator K satisfies the following identity

$$K = \frac{1}{2m} + \frac{1}{2mc^2} V K, \quad (7)$$

which is often used to split off the non-relativistic kinetic energy from the ZORA kinetic energy $\hat{T}_{\text{ZORA}} = (\boldsymbol{\sigma} \cdot \mathbf{p})K(\boldsymbol{\sigma} \cdot \mathbf{p})$ [4,9].

Let us introduce an auxiliary orthonormal basis set $\boldsymbol{\phi}$ for the use in the spectral RI operator $\hat{I} = \boldsymbol{\phi}\boldsymbol{\phi}^\dagger$

$$\boldsymbol{\phi} = (\boldsymbol{\sigma} \cdot \mathbf{p})\boldsymbol{\chi} \frac{\mathbf{T}^{-1/2}}{(2m)^{1/2}}. \quad (8)$$

In Eq. (8) \mathbf{T} is the matrix of the kinetic energy operator

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

A similar auxiliary basis set was used previously by Faas et al. [7].

Using the hermiticity property of the $(\boldsymbol{\sigma} \cdot \mathbf{p})$ operator and Eq. (7), the elements of the ZORA kinetic energy matrix \mathbf{K}_1 can be written as in Eq. (9).

$$\begin{aligned} (\mathbf{K}_1)_{\mu\nu} &= \frac{1}{2m} \left\langle (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\mu \left| \frac{1}{1 - \frac{V}{2mc^2}} \right| (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\nu \right\rangle \\ &= \mathbf{T}_{\mu\nu} + \frac{1}{2mc^2} \langle (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\mu |VK| (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\nu \rangle. \end{aligned} \quad (9)$$

With the help of the RI operator with the auxiliary basis $\boldsymbol{\phi}$ Eq. (9) can be rewritten as

$$(\mathbf{K}_1)_{\mu\nu} = \mathbf{T}_{\mu\nu} + (\mathbf{W}_0\mathbf{T}^{-1}\mathbf{K}_1)_{\mu\nu}, \quad (10)$$

where \mathbf{W}_0 is the matrix with elements given in Eq. (11)

$$(\mathbf{W}_0)_{\mu\nu} = \left\langle (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\mu \left| \frac{V}{4m^2c^2} \right| (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\nu \right\rangle. \quad (11)$$

Eq. (10) can be solved in matrix form for the matrix \mathbf{K}_1 . First let us represent \mathbf{K}_1 as

$$\mathbf{K}_1 = \mathbf{T} + \mathbf{W}. \quad (12)$$

Substituting Eq. (12) into Eq. (10) one gets Eq. (13).

$$\mathbf{W} = \mathbf{W}_0 + \mathbf{W}_0\mathbf{T}^{-1}\mathbf{W}. \quad (13)$$

Multiplying Eq. (13) with matrix \mathbf{W}_0^{-1} from the left and with \mathbf{W}^{-1} from the right, one has for the matrix \mathbf{W} Eq. (14).

$$\mathbf{W}^{-1} = \mathbf{W}_0^{-1} - \mathbf{T}^{-1}. \quad (14)$$

The elements of the \mathbf{K}_2 matrix, which appears in the normalization term on the RHS of the IORA Eq. (5) with the help of Eq. (15)

$$\begin{aligned} 2mK^2 &= \frac{1}{2m} \frac{1}{\left(1 - \frac{V}{2mc^2}\right)^2} \\ &= \frac{1}{2m} + \frac{1}{mc^2}VK + 2mK \frac{V}{2mc^2} \frac{V}{2mc^2}K \end{aligned} \quad (15)$$

can be transformed to Eq. (16).

$$\begin{aligned} 2m^2(\mathbf{K}_2)_{\mu\nu} &= \langle (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\mu |2mK^2| (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\nu \rangle \\ &= \mathbf{T}_{\mu\nu} + 2 \left\langle (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\mu \left| \frac{V}{2mc^2}K \right| (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\nu \right\rangle \\ &\quad + 2m \left\langle (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\mu \left| K \frac{V}{2mc^2} \frac{V}{2mc^2}K \right| (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\nu \right\rangle. \end{aligned} \quad (16)$$

As follows from Eqs. (9) and (12), the integrals $\langle (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\mu | \frac{V}{2mc^2}K | (\boldsymbol{\sigma} \cdot \mathbf{p})\chi_\nu \rangle$ are the elements of the \mathbf{W} matrix. Using the RI operator with the auxiliary basis $\boldsymbol{\phi}$ in the third line of Eq. (16), the matrix \mathbf{K}_2 can be represented as

$$\mathbf{K}_2 = \frac{1}{2mc^2}(\mathbf{T} + 2\mathbf{W} + \mathbf{W}\mathbf{T}^{-1}\mathbf{W}). \quad (17)$$

Thus, the matrices \mathbf{K}_1 and \mathbf{K}_2 , which are necessary to perform ZORA and IORA calculations can easily be calculated from Eqs. (12)–(14) and (17). The elements of the \mathbf{W}_0 matrix can be expressed in terms of the usual molecular integrals and can be calculated with the help of the standard non-relativistic quantum-chemical programs. Consequently, the use of the RI as given in Eqs. (12)–(14) and (17) does not require the calculation of molecular integrals other than used in the standard non-relativistic calculation. Also, at variance with the previous implementations [6–9] of the RI technique, the auxiliary basis set defined in Eq. (8) does not appear explicitly in the final formulae for \mathbf{K}_1 and \mathbf{K}_2 .

The accuracy of our final formulae, Eqs. (12)–(14) and (17), has been tested in the calculations on H-like atomic ions. The calculations employed a basis set of 62 s-type Gaussian functions with exponential parameters $\alpha_i = Z^2\alpha'_i$, where $\alpha'_i = 8 \times 10^{-8}, 1 \times 10^{-7}, 2 \times 10^{-7}, 4 \times 10^{-7}, \dots, 8 \times 10^7, 1 \times 10^8$ [12]. In Table 1 the results of our RI-ZORA and RI-IORA calculations for low-lying

$ns_{1/2}$ -states of U^{91+} ion are compared with the numerical results from [5]. The error introduced by the use of the RI technique is of the order 10^{-4} hartree. A somewhat larger deviation of the $4s_{1/2}$ orbital energy from the target value is of the same order of magnitude as obtained in the non-relativistic calculation with the same basis set (exact: -264.5000 hartree, basis set: -264.4961 hartree).

2.2. Gauge dependence

If a computational scheme is gauge invariant, then shifting the potential V by a certain amount Δ will result in exactly the same shift in eigenenergies [3–5,8,9]. The ZORA method is not gauge invariant, as the shift in its eigenenergies deviates from the potential shift by [3–5,9]

$$E_0^{\text{ZORA}} - E_{\Delta}^{\text{ZORA}} + \Delta \approx \frac{E_0^{\text{ZORA}} \Delta}{2mc^2}. \quad (18)$$

The IORA method is also not gauge invariant, but possesses much lesser degree of non-invariance [5,9]

$$E_0^{\text{IORA}} - E_{\Delta}^{\text{IORA}} + \Delta \approx -\frac{(E_0^{\text{IORA}})^2 \Delta}{4m^2 c^4}. \quad (19)$$

Although such a gauge dependence may seem weak, for heavy nuclei it still results in quite large deviation from the exact behavior [9]. In molecules, a role of the gauge shift Δ play tails of the potentials of the neighboring nuclei. As the nuclei get closer to one another, the corresponding shift becomes more negative and the ZORA (or IORA) energy decreases faster than it should. Consequently, a correction for the gauge dependence is necessary when calculating the relative energies

and the energy derivatives with respect to coordinates of nuclei (see e.g. [3,4]).

However, as Eqs. (18) and (19) suggest, the change of the wavefunction metric from the non-relativistic one in ZORA Eq. (1) to a quasi-relativistic metric of IORA reduces the erroneous gauge dependence by almost two orders of magnitude. It seems quite natural to investigate if a modification of the IORA quasi-relativistic metric can reduce the gauge error even further.

The second term in parentheses on the RHS of Eq. (2) can be represented as in Eq. (20).

$$\frac{K^2}{c^2} = \frac{1}{4m^2 c^2} \frac{1}{(1 - \frac{V}{2mc^2})^2} = \frac{K}{2mc^2} + \frac{V}{2mc^4} K^2. \quad (20)$$

Let us consider the behavior of the K^2/c^2 and $K/(2mc^2)$ operators in two limiting cases, extremely weak potential ($V \rightarrow 0$) and infinitely strong potential ($V \rightarrow -\infty$). This reveals that in the two cases both operators possess common limits given in Eq. (21).

$$\lim_{V \rightarrow 0} \frac{K^2}{c^2} = \lim_{V \rightarrow 0} \frac{K}{2mc^2} = \frac{1}{4m^2 c^2}, \quad (21)$$

$$\lim_{V \rightarrow -\infty} \frac{K^2}{c^2} = \lim_{V \rightarrow -\infty} \frac{K}{2mc^2} = 0.$$

Thus, at the two asymptotes the IORA Eq. (2) is equivalent to Eq. (22),

$$\left(\frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{1}{1 - \frac{V}{2mc^2}} (\boldsymbol{\sigma} \cdot \mathbf{p}) + V \right) \psi$$

$$= \epsilon \left(1 + \frac{1}{4m^2 c^2} (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{1}{1 - \frac{V}{2mc^2}} (\boldsymbol{\sigma} \cdot \mathbf{p}) \right) \psi, \quad (22)$$

where the K^2/c^2 operator in the normalization term is replaced by the $K/(2mc^2)$.

Table 1
ZORA, IORA and Dirac spinor energies of U^{91+}

Spinor	ZORA ^a	RI-ZORA ^b	IORA ^a	RI-IORA ^b	Dirac
$1s_{1/2}$	-722.7448	-722.7438	-59.9013	-59.9006	-4861.1980
$2s_{1/2}$	-43.5545	-43.5543	-1.1385	-1.1383	-1257.3959
$3s_{1/2}$	-7.8507	-7.8498	-0.0957	-0.0948	-539.0933
$4s_{1/2}$	-2.3395	-2.3356	-0.0163	-0.0123	-295.2578

The absolute Dirac eigenenergies (in hartrees) are given. For the other methods the difference from the Dirac energy is reported, $\Delta E^{\text{method}} = E^{\text{method}} - E^{\text{Dirac}}$.

^a Numeric results from [5].

^b Present work, with the use of resolution of the identity.

An interesting feature of Eq. (22) is that the leading term in the expansion of gauge shift error $E_0^{\text{Eq. (22)}} - E_{\Delta}^{\text{Eq. (22)}} + \Delta$ has the same magnitude as for the IORA method (see Eq. (19)), however with the opposite sign. The gauge dependence of Eq. (22) can be established by substituting $V + \Delta$ instead of V and expanding both sides of the equation in power series with respect to $\Delta/2mc^2$. Up to a leading term, the gauge dependence of Eq. (22) is given by Eq. (23),

$$\begin{aligned} E_0^{\text{Eq. (22)}} - E_{\Delta}^{\text{Eq. (22)}} + \Delta & \\ & \approx -\frac{\Delta}{mc^4} \left\langle (\boldsymbol{\sigma} \cdot \mathbf{p}) \psi \left| \left(\frac{V}{2} \right) K_0^2 \right| (\boldsymbol{\sigma} \cdot \mathbf{p}) \psi \right\rangle \\ & \quad + \frac{E_0^{\text{Eq. (22)}} \Delta}{2mc^4} \langle (\boldsymbol{\sigma} \cdot \mathbf{p}) \psi | K_0^2 | (\boldsymbol{\sigma} \cdot \mathbf{p}) \psi \rangle \\ & \approx + \frac{(E_0^{\text{Eq. (22)}})^2 \Delta}{4m^2 c^4}, \end{aligned} \quad (23)$$

where K_0 stands for K from Eq. (6) calculated without shift in the potential V . The third line of Eq. (23) is obtained by replacing $V/2$ with its average value from the non-relativistic virial theorem and estimating the remaining matrix elements as in Eq. (46) of [5].

Thus, a considerable reduction in the erroneous gauge dependence of the IORA eigenenergy can be achieved if the normalization terms in Eqs. (2) and (22) are combined with equal weights. As it is obvious from Eq. (21), such a combined equation will be essentially equivalent to the original IORA equation at two asymptotes, $V \rightarrow 0$ and $V \rightarrow -\infty$. The choice of the weighting factors, $1/2$ and $1/2$, is dictated by Eqs. (19) and (23), rather than empirical reasons.

The combined method, dubbed IORamm (IORA with modified metric), is given in Eq. (24)

$$\begin{aligned} & \left(\frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{1}{1 - \frac{V}{2mc^2}} (\boldsymbol{\sigma} \cdot \mathbf{p}) + V \right) \psi \\ & = \epsilon \left(1 + \frac{1}{8m^2 c^2} (\boldsymbol{\sigma} \cdot \mathbf{p}) \right. \\ & \quad \left. \times \left(\frac{1}{1 - \frac{V}{2mc^2}} + \frac{1}{(1 - \frac{V}{2mc^2})^2} \right) (\boldsymbol{\sigma} \cdot \mathbf{p}) \right) \psi \end{aligned} \quad (24)$$

and in matrix form in Eq. (25)

$$\begin{aligned} & (\mathbf{V} + \mathbf{T} + \mathbf{W}) \mathbf{C} \\ & = \left(\mathbf{S} + \frac{1}{2mc^2} \left(\mathbf{T} + \frac{3}{2} \mathbf{W} + \frac{1}{2} \mathbf{W} \mathbf{T}^{-1} \mathbf{W} \right) \right) \mathbf{C} \epsilon \end{aligned} \quad (25)$$

where \mathbf{W} is given in Eq. (14). Numeric calculations with the new method performed with the aforementioned basis of 62 Gaussian functions [12] for the ground state of H-like uranium ion confirm the conclusions from the above analysis and show that the erroneous gauge dependence of the energy from IORamm is reduced by more than an order of magnitude compared to the IORA method. For example, with the gauge shift $\Delta = -10$ a.u. (value typical for molecular systems) the gauge error $E_0 - E_{\Delta} + \Delta$ from IORamm is only 0.0162 a.u. as compared to 0.2250 a.u. from the original IORA method. In the next section, it will be demonstrated that the use of the IORamm method in molecular calculations does not result in noticeable distortions of the molecular structure even if no corrections for the residual gauge dependence of the energy is applied.

2.3. Many-electron systems

In the case of many-electron systems, full ZORA and IORA equations include not only the Coulomb and exchange contributions to the total potential V , but also the exchange two-electron terms between the large and small components of the quasi-relativistic wavefunction, which appear together with the linear momentum operator \mathbf{p} [6–9]. Thus, a large number of additional two-electron integrals must be calculated compared to the non-relativistic case. These complications can be avoided if only the one-electron Hamiltonian in the Hartree–Fock equations is treated relativistically. Such a one-electron approximation has proved [13–15] to be capable of reproducing the scalar relativistic effects on energetic properties with accuracy sufficient for chemical applications. The scalar relativistic (one-component) approximation amounts to omitting all spin–orbit terms in ZORA and IORA equations and is achieved by replacing the $(\boldsymbol{\sigma} \cdot \mathbf{p})$ operator with the linear mo-

momentum operator \mathbf{p} . In case of the IORA or IORAm methods, the one-electron Hamiltonian, given in Eqs. (5), (12) and (25), has to be renormalized as given in Eq. (26),

$$\mathbf{H}' = (\mathbf{S}^{1/2})^\dagger (\mathbf{X}^{-1/2})^\dagger (\mathbf{V} + \mathbf{T} + \mathbf{W}) (\mathbf{X}^{-1/2}) (\mathbf{S}^{1/2}), \quad (26)$$

where the matrix X for IORA and IORAm is given by Eqs. (27a) and (27b), respectively.

$$\mathbf{X} = \mathbf{S} + \frac{1}{2mc^2} (\mathbf{T} + 2\mathbf{W} + \mathbf{W}\mathbf{T}^{-1}\mathbf{W}), \quad (27a)$$

$$= \mathbf{S} + \frac{1}{2mc^2} (\mathbf{T} + \frac{3}{2}\mathbf{W} + \frac{1}{2}\mathbf{W}\mathbf{T}^{-1}\mathbf{W}). \quad (27b)$$

Thus, the Hartree–Fock equations within the scalar relativistic one-electron approximation read

$$(\mathbf{H}' + \mathbf{J}_i - \mathbf{K}_i)\mathbf{C}_i = \mathbf{S}\mathbf{C}_i\epsilon_i, \quad (28)$$

where \mathbf{J}_i and \mathbf{K}_i are the usual non-relativistic Coulomb and exchange matrices. The use of the one-electron approximation in many-electron calculations with the regular quasi-relativistic Hamiltonians has an additional advantage that the potential V in the denominator does not depend on the electron repulsion. Had it been opposite, it would have created problems with the calculation of ionization energies because of the lack of gauge invariance in methods based on the regular approximation [3].

3. Details of calculations

The described RI-ZORA, RI-IORA and RI-IORAm, Eqs. (12), (14), (17), (25–28), were implemented into the COLOGNE 2001 suite of quantum-chemical programs [16]. Currently only single-point SCF and post-SCF calculations are available, such that all optimizations of molecular structures reported in the Letter were done numerically. The RI-ZORA/SCF, RI-IORA/SCF and RI-IORAm/SCF calculations have been done for noble gas atoms He–Xe. Since, the ZORA method has severe problems with gauge invariance, the molecular calculations have been done only with RI-IORA and RI-IORAm methods. Benchmark calculations were carried out for diatomic molecules AgH and Ag₂ and for

polyatomic molecules WF₆ and WCl₆. The molecular calculations have been done at the SCF and MP2 (with all valence electrons correlated) levels of theory. The basis set superposition error is taken into account when calculating the molecular atomization energies.

The TZV basis set of Ahlrichs [17] was used for noble gas atoms He through Kr. For Xe atom the uncontracted basis set of Dyllal was employed [18]. The calculations on silver compounds employed uncontracted basis set derived from the basis set of Gropen [19] and augmented by one diffuse s-, three diffuse p-, and two diffuse d-type functions in an even-tempered sequence with ratio 2.5. The resulting (18s15p10d) basis set was combined with Dunning's aug-cc-pVTZ basis set [20] for hydrogen.

For tungsten compounds the partially decontracted basis set of Gropen [19] was used. The innermost three and the outermost eight s-type functions were uncontracted. The remaining s-functions were block contracted in the pattern (3/2/2/2) using the contraction coefficients for the 1s-, 2s-, 3s- and 4s-orbitals. The outermost five p-type orbitals were uncontracted and the rest of p-orbitals was block contracted in the pattern (3/3/2/2) using the contraction coefficients for the 2p-, 3p-, 4p- and 5p-orbitals. The 5d-orbital and the outermost primitive Gaussian d-orbital of the original basis set were dropped due to orthogonality problem. The remaining two outermost orbitals were uncontracted and the rest of d-orbitals was contracted by scheme (4/2/2) taking the contraction coefficients from the 3d-, 3d- and 4d-orbitals, respectively. The outermost two f-type orbitals were uncontracted. Finally, one s-, three p- and d-, and one f-type diffuse functions were added in an even-tempered sequence with ratio 2.5. The resulting block-contracted [16s12p8d6f] basis set was combined with Dunning's aug-cc-pVDZ basis sets [20] on fluorine and chlorine.

4. Results and discussion

First, the gauge dependence of the ZORA, IORA, and IORAm energies is studied in calculations on noble gas atoms He through Xe. Table 2 reports the results. The negative constant

Table 2

Gauge error $E_0^{\text{method}} - E_{\Delta}^{\text{method}} + \Delta$ in the ground-state energy of noble gas atoms for different methods

Atom	RI-ZORA	RI-IOA	RI-IOAmm
He	0.003803	0.000006	0.000003
Ne	0.034280	0.000084	0.000023
Ar	0.077076	0.000464	0.000097
Kr	0.199988	0.003781	0.000628
Xe ^a	0.375149	0.014135	0.001853

The gauge error is given in hartrees. The gauge shift Δ is chosen such that the total non-relativistic energy is shifted by exactly -100 hartrees. Calculations employ the TZV basis set of Ahlrichs [17] unless noted otherwise.

^a Calculated with uncontracted relativistic basis set from [18].

Δ , which was added to the potential $-Z/r$ is chosen such that the non-relativistic total energy is shifted by exactly -100 hartrees. The same settings were used in [9] when investigating the gauge dependence of ZORA and IOA. The results in Table 2 confirm the conclusion that IOAmm has about an order of magnitude weaker gauge dependence than IOA. As will be demonstrated further, such a gauge error does not result in serious distortion of optimized molecular structure.

Table 3 compares the orbital energies from RI-ZORA, RI-IOA and RI-IOAmm calculations for Xe atom with the results of the Dirac–Fock calculations performed in [7] with the same basis set. The comparison shows that the IOAmm method reproduces closely the Dirac–Fock (DF) results. Generally, the IOAmm orbital energies are slightly above the DF values, whereas the IOA method yields more negative orbital ener-

gies. However, an overall accuracy of the results from the two methods is basically the same with very good agreement in the valence and sub-valence shells and reasonable agreement (deviations less than 1 hartree) in the deep core region.

Table 4 presents the results of IOA and IOAmm calculations for di- and polyatomic molecules performed at the SCF and MP2 levels. Since, both methods, IOA and IOAmm, are not completely gauge invariant, the energy differences must be corrected for the gauge error. The gauge error arises from an incorrect response of the orbitals on atom A to the potentials of other nuclei in molecule. Thus, the effect of such an error can be compensated in the atomic calculation; when calculating the total IOA or IOAmm energy of an atom, the constant negative shift must be introduced, which is the value of the potentials of other atoms in the molecule at the

Table 3

Orbital energies for xenon atom obtained with Dirac–Fock, ZORA, IOA and IOAmm methods

Orbital	Dirac–Fock ^a	RI-ZORA	RI-IOA	RI-IOAmm
1s	-1277.2511	-1338.8489	-1278.8691	-1276.4954
2s	-202.4603	-205.6187	-202.4880	-202.3727
2p	-181.6912	-184.1154	-181.5652	-181.5234
3s	-43.0057	-43.4147	-43.0148	-42.9998
3p	-36.0988	-36.3625	-36.0818	-36.0773
3d	-25.7266	-25.8598	-25.7330	-25.7341
4s	-8.4255	-8.4889	-8.4283	-8.4257
4p	-6.1350	-6.1644	-6.1321	-6.1316
4d	-2.6604	-2.6608	-2.6613	-2.6617
5s	-1.0070	-1.0129	-1.0073	-1.0070
5p	-0.4541	-0.4544	-0.4535	-0.4535

Calculations employ the uncontracted relativistic basis set from [18].

^a Results of Dirac–Fock calculations from [7] performed with the same basis set. p- and d-orbital energies are averaged over spin-orbit components.

Table 4
Optimized structures, vibrational frequencies and dissociation energies of some diatomic and polyatomic molecules

Molecule	Method	r_e (Å)	ω_e (cm ⁻¹)	ΔE_e^a (eV)	ΔH_{298}° ^b (kcal/mol)
AgH	RI-IORA/SCF	1.695	1623	1.15	
	RI-IORAmM/SCF	1.697	1621	1.15	
	DHF/SCF ^c	1.700	1605	1.23	
	RI-IORA/MP2	1.590	1805	2.07	
	RI-IORAmM/MP2	1.592	1799	2.07	
	DHF/MP2 ^e	1.598	1832	2.14	
	exp. ^d	1.618	1760	2.39	
Ag ₂	RI-IORA/SCF	2.542	199	0.36	
	RI-IORAmM/SCF	2.662	160	0.42	
	RI-IORA/MP2	2.472	227	1.20	
	RI-IORAmM/MP2	2.566	190	1.27	
	exp. ^d	2.531	192	1.67	
WF ₆	RI-IORA/SCF	1.790		19.66	
	RI-IORAmM/SCF	1.810		19.74	
	RI-IORA/MP2	1.806		32.54	731 ^e
	RI-IORAmM/MP2	1.829		32.67	734 ^e
	exp.	1.829 ^f			729 ^g
WCl ₆	RI-IORA/SCF	2.238		10.82	
	RI-IORAmM/SCF	2.282		11.06	
	RI-IORA/MP2	2.232		20.68	
	RI-IORAmM/MP2	2.282		21.03	
	exp.	2.289 ^h			

^a Atomization energy. Corrected for basis set superposition error (BSSE) and gauge dependence error (see text for details).

^b Atomization enthalpy.

^c From Ref. [22].

^d From Ref. [23].

^e Calculated from atomization energies with inclusion of spin-orbit (−15.6 kcal/mol) and zero-point and thermal vibrational (−4 kcal/mol) corrections taken from [24].

^f From Ref. [25].

^g From Ref. [24].

^h From Ref. [26].

position of the given atom. The gauge non-invariance error $E_0 - E_\Delta + \Delta$ is the difference between the total atomic energy obtained without shift (E_0) and the total energy (E_Δ) calculated with shift Δ in the nuclear potential. The latter calculation employs the wavefunction from the former calculation and does not optimize it. Generally speaking, this is a variant of the electrostatic shift approximation (ESA) used in ZORA calculations [3,4] and is similar to counterpoise correction for the basis set superposition error [21]. Since, IORA and IORAmM possess much weaker gauge dependence than ZORA, no corrections to the total energies are used during the geometry optimizations.

Comparison of the IORAmM results with the target values (experimental or theoretical) shows that the effect of the gauge dependence on the optimized molecular structures is extremely weak. In the case of AgH, the RI-IORAmM/MP2 gauge error is only 0.0001881 hartree for Ag and is less by about an order of magnitude than the error of 0.0014038 hartree from the RI-IORA/MP2 calculation. The effect of such an error on the energy derivative with respect to the nuclear coordinates is of the order of 10^{-5} hartree/bohr for IORAmM and is beyond the threshold of tolerance for the energy gradient in the optimization routines (ca. 10^{-4} hartree/bohr). Such that the results of both IORA and IORAmM optimizations of AgH

structure are not affected by the gauge dependence. The agreement of the IORA and IORAm results with the Dirac–Hartree–Fock values is reasonably good at both SCF and MP2 levels of theory.

For Ag₂ molecule the discrepancy between the IORA and IORAm results is larger than for AgH. The IORA results are clearly affected by the method's gauge non-invariance. The gauge error for Ag atom due to the proximity to another Ag nucleus is 0.0430799 hartree from the RI-IORA/MP2 calculation whereas it is only 0.0054976 hartree from the RI-IORAm/MP2 calculation. Since, no correction for the gauge dependence was included during the geometry optimization, the Ag–Ag bond length from the IORA calculation is markedly shorter. At the same time the RI-IORAm results are in reasonable agreement with the experimental data.

The same trend is observed for polyatomic molecules. The W–F and W–Cl bond lengths from IORA calculations are shorter than from IORAm. Again, the gauge error in the RI-IORA/MP2 calculations (0.4133119 hartree for WF₆ and 0.6335881 hartree for WCl₆) is more than an order of magnitude larger than in RI-IORAm/MP2 (0.0151375 hartree for WF₆ and 0.0238426 hartree for WCl₆). It should be noted that the IORAm gauge error is of the same order of magnitude as (and even less than) the basis set superposition error (BSSE RI-IORAm/MP2: 0.064529 hartree for WF₆ and 0.0549552 hartree for WCl₆). Such that the neglect of the gauge non-invariance correction in the geometry optimization has nearly the same effect on the results as the neglect of BSSE.

In the last column of Table 4, the atomization enthalpies for WF₆ calculated with the RI-IORA/MP2 and RI-IORAm/MP2 methods are presented. The effect of the spin–orbit interaction (–15.6 kcal/mol) on the atomization energy of WF₆ and the zero-point and thermal vibrational corrections (4 kcal/mol) are taken from [24] where the WF₆ dissociation has been studied with the help of RECP-B3LYP calculations. The atomization enthalpies from both methods, RI-IORA/MP2 and RI-IORAm/MP2, compare well with the experimental datum. At the same time only the RI-IORAm/MP2 lengths for the W–F and W–Cl bonds are in good agreement with the experiment.

5. Conclusions

A compact representation for the matrix elements of the ZORA and IORA regular approximation Hamiltonians is proposed. The representation uses RI, however no additional molecular integrals, which involve an auxiliary basis set used in the RI appear in final formulae for the Hamiltonian matrix elements. The new technique is easy to implement in the standard non-relativistic quantum chemical codes and provides good accuracy compared to the numeric ZORA and IORA results.

An approximate solution to the gauge dependence of the IORA total energy is proposed. The use of the modified quasi-relativistic metric in the IORAm (IORA with modified metric) method reduces considerably (ca. an order of magnitude) the erroneous gauge dependence of the total energy. The benchmark calculations show that the residual gauge error in IORAm is approximately equal to or less than the basis set superposition error. Thus, its effect on the optimized molecular structures is relatively small. The IORAm calculations performed at the SCF and MP2 level for AgH, Ag₂, WF₆ and WCl₆ molecules demonstrate that the new quasi-relativistic method yields molecular structures and atomization energies (calculated with account of the gauge error) in close agreement with the experiment. At the same time, the computational cost of the IORAm calculation is essentially the same as the cost of the standard non-relativistic all electron calculation.

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