Representation of the exact relativistic electronic Hamiltonian within the regular approximation

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The exact relativistic Hamiltonian for electronic states is expanded in terms of energy-independent linear operators within the regular approximation. An effective relativistic Hamiltonian has been obtained, which yields in lowest order directly the infinite-order regular approximation (IORA) rather than the zeroth-order regular approximation method. Further perturbational expansion of the exact relativistic electronic energy utilizing the effective Hamiltonian leads to new methods based on ordinary (IORAn) or double [IORA$n(2)$] perturbation theory (n: order of expansion), which provide improved energies in atomic calculations. Energies calculated with IORA4 and IORA3(2) are accurate up to c^{-20}. Furthermore, IORA is improved by using the IORA wave function to calculate the Rayleigh quotient, which, if minimized, leads to the exact relativistic energy. The outstanding performance of this new IORA method coined scaled IORA is documented in atomic and molecular calculations. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1623473]

I. INTRODUCTION

The all-electron methods derived on the basis of the regular approximation (RA) to the exact relativistic Dirac equation are among the most used computational tools designed for a relativistic description of atomic and molecular systems.[1–16] The zeroth-order,[1,2] first-order,[2] and infinite-order[8] regular approximations (ZORA, FORA, and IORA, respectively) as well as the expansions and modifications derived therefrom[12,13] have proven to be very useful methods because they can lead to high accuracy results for molecules containing heavy atoms.

The concept of the regular approximation is based on the expansion of the exact Foldy–Wouthuysen transformation[17] of the Dirac Hamiltonian with respect to a parameter $E/(2mc^2-V)$ that depends on both the energy E and the potential V.[1,2,8] The use of a potential-dependent parameter leads to a perturbational expansion that does not possess the singularity problems typical of the standard expansion in terms of $1/c^2$ (thus the name regular approximation).[1,2,8] However, prior to expansion, the exact relativistic Hamiltonian has to be brought into an energy-dependent form, which is valid only as long as it operates on the exact relativistic eigenfunction.

At the lowest order in this expansion one obtains the ZORA Hamiltonian,[1,2] which is bound from below[3] and can be used in (quasi)variational calculations. The ZORA eigenvalues are lower than the exact relativistic energies.[1–3] Within the variational formalism, an improvement can be achieved[8] by including the lowest order correction to the metric, on which the relativistic wave function is normalized. This leads to the IORA method.[8] ZORA and IORA are the only (quasi)variational methods within the regular approximation. Further improvement of the ZORA or IORA energy can only be achieved perturbatively.[2,8] This is not surprising,

because, in the now standard approach to the regular approximation, the exact relativistic Hamiltonian for electronic (positive-energy) states is represented in the energy-dependent form. The expansion of such a Hamiltonian in powers of the perturbational parameter will contain the (power of) energy eigenvalue in all orders except the lowest.

For the purpose of going beyond the ZORA and IORA methods and of finding a way for a variational improvement of the energy within the RA, one needs to know the expansion of the exact relativistic Hamiltonian in terms of linear energy-independent operators rather than energy eigenvalues. This goal cannot be achieved if one starts from the energy-dependent relativistic Hamiltonian. The energy-independent exact relativistic Hamiltonian for positive (electronic) energy states is not known in closed algebraic form, except for the trivial case of a free particle.[17] The construction of an expansion of the exact Hamiltonian, only in terms of linear operators, has been attempted in many investigations,[18–23] of which the one by Heully *et al.*[18] and the one by Chang *et al.*[19] are commonly cited as the cornerstones of the RA. In both investigations, the ZORA Hamiltonian was obtained in the lowest order of the expansion (note that the terms regular approximation and ZORA were suggested later by Baerends *et al.*[2]). However, in these studies the expansion of the exact Hamiltonian was either truncated at the low-order terms[18] or pursued with the different goal of obtaining an effective relativistic Hamiltonian in the recursive form $\hat{H}^{\mathrm{eff}}=f(\hat{H}^{\mathrm{eff}})$.[19]

In the present work, we report a derivation of a regular expansion of the exact relativistic Hamiltonian for electronic states in terms of linear energy-independent operators. In this expansion, certain terms are summed up to infinite order and an expression for the effective energy-independent relativistic Hamiltonian is derived. In the lowest order, the effective

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Hamiltonian thus obtained leads directly to the IORA rather than the ZORA method. A perturbational expansion of the exact relativistic electronic energy based on the new effective Hamiltonian is constructed and investigated. Formulas up to fourth order are derived, implemented in the IORA approach, and tested for atomic calculations. Further improvements are gained by calculating with the IORA wave function the Rayleigh quotient that, if minimized, would lead to the exact formalism. The new quasirelativistic method, which we shall call scaled IORA (SIORA), is tested in atomic and molecular calculations and is found to lead to considerable improvements in the relativistically corrected energies.

II. BASIC THEORY OF THE RELATIVISTIC ELECTRONIC HAMILTONIAN

The Dirac equation for a single electron moving in a potential V is given by[24]

$$\hat{H}_D \psi_i^D = \begin{pmatrix} V & c(\boldsymbol{\sigma}\cdot\mathbf{p}) \\ c(\boldsymbol{\sigma}\cdot\mathbf{p}) & V-2mc^2 \end{pmatrix} \begin{pmatrix} \psi_i^L \\ \psi_i^S \end{pmatrix} = \epsilon_i \begin{pmatrix} \psi_i^L \\ \psi_i^S \end{pmatrix}. \quad (1)$$

In Eq. (1), $\boldsymbol{\sigma}$ is the vector of the Pauli matrices $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$,[25] $\mathbf{p} = -i\hbar\nabla$ is the momentum operator, m is the rest mass of electron, and c is the velocity of light. Equation (1) describes simultaneously particle and antiparticle (i.e., electronic and positronic) states, which are, in general, superpositions of the large-component ψ_i^L and the small-component ψ_i^S wave functions. For the description of chemical systems, knowledge of electronic solutions of Eq. (1) is sufficient and one usually proceeds with a decoupling of the two types of solutions from each other. In the most general case, this can be achieved with the help of a Foldy–Wouthuysen (FW) transformation[17] given in Eq. (2), which, upon applying to the Dirac Hamiltonian $\hat{H}_D$, leads[17,20,21] to a partitioning into two Hermitian operators $\hat{H}_+$ and $\hat{H}_-$ for electronic and positronic states, respectively,

$$\hat{U}_{FW}\hat{H}_D\hat{U}_{FW}^{-1}(\hat{U}_{FW}\psi_i^D) = \begin{pmatrix} \hat{H}_+ & 0 \\ 0 & \hat{H}_- \end{pmatrix} \begin{pmatrix} \phi_i^{FW} \\ 0 \end{pmatrix} = \epsilon_i \begin{pmatrix} \phi_i^{FW} \\ 0 \end{pmatrix}. \quad (2)$$

The unitary operator $\hat{U}_{FW}$, which carries out the FW transformation, has been described in many publications[1,2,8,20,21] and its detailed form is not reproduced here for brevity. This operator is parametrized in terms of another (non-Hermitian) operator $\hat{X}$, which satisfies

$$c(\boldsymbol{\sigma}\cdot\mathbf{p}) = 2mc^2\hat{X} + [\hat{X},V] + \hat{X}c(\boldsymbol{\sigma}\cdot\mathbf{p})\hat{X} \quad (3)$$

and connects the large and the small components of the Dirac wave function ψ_i^D via the following:[1,2,8,20,21]

$$\psi_i^S = \hat{X}\psi_i^L. \quad (4)$$

In the general case, the exact solution of Eq. (3) is not known in a closed algebraic form and the same is true for the operators $\hat{U}_{FW}$ and $\hat{H}_+$. Perturbational expansions of the operators $\hat{H}_+$ and $\hat{U}_{FW}$ suggested in the literature[18,20–23] are very complicated and one usually truncates these expansions at the lowest orders.

It has been suggested[21] that the use of a similarity transformation (change of the basis set used to construct a linear operator) carried out with the help of a non-Hermitian operator $\hat{\gamma}$,

$$\hat{\gamma} = \begin{pmatrix} 1 & 0 \\ \hat{X} & 1 \end{pmatrix}, \quad \hat{\gamma}^{-1} = \begin{pmatrix} 1 & 0 \\ -\hat{X} & 1 \end{pmatrix}, \quad (5)$$

results in simpler algebraic expressions for the transformed Dirac equation,

$$\hat{\gamma}^{-1}\hat{H}_D\hat{\gamma}(\hat{\gamma}^{-1}\psi_i^D)$$
$$= \begin{pmatrix} V+c(\boldsymbol{\sigma}\cdot\mathbf{p})\hat{X} & c(\boldsymbol{\sigma}\cdot\mathbf{p}) \\ 0 & V-\hat{X}c(\boldsymbol{\sigma}\cdot\mathbf{p})-2mc^2 \end{pmatrix} \begin{pmatrix} \psi_i^L \\ 0 \end{pmatrix}$$
$$= \epsilon_i \begin{pmatrix} \psi_i^L \\ 0 \end{pmatrix}. \quad (6)$$

In Eq. (6), the small-component wave function ψ_i^S is eliminated and the large-component wave function is a solution of Eq. (7) with the non-Hermitian effective Hamiltonian $\hat{L}$, which has the positive-energy eigenvalues of $\hat{H}_D$ as its eigenvalues, ψ_i^L as its right eigenfunctions, and $(\psi_i^L)^\dagger + (\psi_i^S)^\dagger\hat{X}$ as its left eigenfunctions,

$$\hat{L}\psi_i^L = (V+c(\boldsymbol{\sigma}\cdot\mathbf{p})\hat{X})\psi_i^L = \epsilon_i\psi_i^L. \quad (7)$$

Rewriting Eq. (3) in form of Eq. (8) establishes a connection between the operator $\hat{X}$ and the effective Hamiltonian $\hat{L}$,

$$(2mc^2-V)\hat{X} = c(\boldsymbol{\sigma}\cdot\mathbf{p}) - \hat{X}V - \hat{X}c(\boldsymbol{\sigma}\cdot\mathbf{p})\hat{X}$$
$$= c(\boldsymbol{\sigma}\cdot\mathbf{p}) - \hat{X}\hat{L}. \quad (8)$$

Considering the last term on the right-hand side of Eq. (8) as a perturbation, a perturbational expansion of the effective Hamiltonian $\hat{L}$ was obtained in Ref. 21, whereby it was demonstrated that to the lowest order in $\hat{X}\hat{L}$ the expansion leads to the so-called ZORA (zeroth-order regular approximation) Hamiltonian, $\hat{H}^{ZORA}$ (see the following). No attempts were reported to go beyond the first order in $\hat{X}\hat{L}$, which corresponds to the first-order regular approximation (FORA).

As an alternative to the perturbational expansion one can use the iteration technique.[19] This technique was used earlier by Chang et al.,[19] with the primary objective to derive expressions of the form $\hat{H}^{eff} = f(\hat{H}^{eff})$ for the effective relativistic Hamiltonian $\hat{H}^{eff}$ [see, e.g., $\hat{L}$ in Eq. (7)]. The objective of the present work is however to express the effective Hamiltonian $\hat{L}$ in terms of simple operators such as $\hat{L}^{(0)}$ (see the following), which were used in the perturbational analysis by Kutzelnigg.[20,21]

III. STRUCTURE OF THE EFFECTIVE RELATIVISTIC HAMILTONIAN

Operators $\hat{X}$ and $\hat{L}$ can be represented by a set of coupled nonlinear equations,

$$\hat{X} = Pc(\boldsymbol{\sigma}\cdot\mathbf{p}) - P\hat{X}\hat{L}, \quad (9a)$$

$$\hat{L} = V + c(\boldsymbol{\sigma}\cdot\mathbf{p})\hat{X}, \quad (9b)$$

where P is an abbreviation for the inverse of $2mc^2-V$,

$$P = \frac{1}{2mc^2 - V}. \tag{10}$$

Then, starting from $\hat{X}^{(0)}$ in the following,

$$\hat{X}^{(0)} = Pc(\boldsymbol{\sigma}\cdot\mathbf{p}), \tag{11}$$

one gets for $\hat{L}^{(0)}$,

$$\hat{L}^{(0)} = V + c(\boldsymbol{\sigma}\cdot\mathbf{p})\hat{X}^{(0)} = V + c^2(\boldsymbol{\sigma}\cdot\mathbf{p})P(\boldsymbol{\sigma}\cdot\mathbf{p}) = \hat{H}^{\mathrm{ZORA}}, \tag{12}$$

which demonstrates that $\hat{L}^{(0)}$ is identical to the (Hermitian) ZORA Hamiltonian $\hat{H}^{\mathrm{ZORA}}$. Substituting $\hat{L}^{(0)}$ and $\hat{X}^{(0)}$ into Eq. (9a), one obtains $\hat{X}^{(1)}$, and from $\hat{X}^{(1)}$ one has $\hat{L}^{(1)}$ via Eq. (9b), etc. In general, this iterative procedure can be written as in the following:

$$\hat{X}^{(l+1)} = \hat{X}^{(0)} - P\hat{X}^{(l)}\hat{L}^{(l)}, \tag{13a}$$

$$\hat{L}^{(l+1)} = \hat{L}^{(0)} - c(\boldsymbol{\sigma}\cdot\mathbf{p})P\hat{X}^{(l)}\hat{L}^{(l)}, \tag{13b}$$

where the superscript l marks the iteration step rather than the order of perturbation theory. Obviously, the exact $\hat{L}$ should emerge at $l = \infty$.

Fortunately, there is no need to investigate $\hat{L}^{(\infty)}$ to unravel the structure of the effective Hamiltonian $\hat{L}$. The op-

erator $\hat{L}^{(5)}$ obtained after five iterations is presented in Eq. (A1), where it is expressed in terms of $\hat{L}^{(0)}$ and the operators $\hat{x}$ and $\hat{x}_k$ defined in Eqs. (14) and (15), respectively,

$$\hat{x} = c^2(\boldsymbol{\sigma}\cdot\mathbf{p})P^2(\boldsymbol{\sigma}\cdot\mathbf{p}) = (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(2mc^2 - V)^2}(\boldsymbol{\sigma}\cdot\mathbf{p}), \tag{14}$$

$$\hat{x}_k = c^2(\boldsymbol{\sigma}\cdot\mathbf{p})P^{k+1}(\boldsymbol{\sigma}\cdot\mathbf{p}) = (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(2mc^2 - V)^{k+1}}(\boldsymbol{\sigma}\cdot\mathbf{p}). \tag{15}$$

One can conclude from Eq. (A1) that from iteration to iteration a prefactor $1 - \hat{x} + \hat{x}^2 - \hat{x}^3 + \cdots$ builds up in front of the $\hat{x}_k$ and $\hat{L}^{(0)}$ operators. Realizing that this prefactor sums up to the operator $\hat{N}^{-1}$,

$$\hat{N}^{-1} = 1 - \hat{x} + \hat{x}^2 - \hat{x}^3 + \cdots$$

$$= \frac{1}{1 + \hat{x}} = \left[1 + (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(2mc^2 - V)^2}(\boldsymbol{\sigma}\cdot\mathbf{p}) \right]^{-1}, \tag{16}$$

Eq. (17) for the exact operator $\hat{L}$ can be inferred, where all terms up to the fourth order in $\hat{L}^{(0)}$ are displayed. Generalization to fifth and higher order is straightforward albeit tedious:

$$
\begin{aligned}
\hat{L} = {} & \hat{N}^{-1}\hat{L}^{(0)} + \hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} - \hat{N}^{-1}\hat{x}_3\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} + \hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} \\
& + \hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} + \hat{N}^{-1}\hat{x}_4\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} \\
& + \hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} + \hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} \\
& + \hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} + \hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} \\
& - \hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{x}_3\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} - \hat{N}^{-1}\hat{x}_3\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} \\
& - \hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{x}_3\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} - \hat{N}^{-1}\hat{x}_3\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} \\
& - \hat{N}^{-1}\hat{x}_3\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{x}_2\hat{N}^{-1}\hat{L}^{(0)}\hat{N}^{-1}\hat{L}^{(0)} + \cdots.
\end{aligned} \tag{17}
$$

IV. PERTURBATIONAL TREATMENT OF THE EFFECTIVE RELATIVISTIC HAMILTONIAN

Substituting Eq. (17) into Eq. (7), one has

$$\hat{L}\psi_i^L = (1 + \hat{N}^{-1}\hat{Z})\hat{N}^{-1}\hat{L}^{(0)}\psi_i^L = \epsilon_i\psi_i^L, \tag{18}$$

where the (non-Hermitian) operator $\hat{Z}$ (for brevity not shown explicitly) collects all terms after the first one on the right-hand side of Eq. (17). Note that the factors $\hat{N}^{-1}$ in front of and $\hat{N}^{-1}\hat{L}^{(0)}$ in back of each term in Eq. (17) were moved outside of the operator $\hat{Z}$. For further analysis, it is convenient to multiply Eq. (18) by the operator $\hat{N}$ from the left, which leads to

$$(1 + \hat{Z}\hat{N}^{-1})\hat{L}^{(0)}\psi_i^L = \epsilon_i\hat{N}\psi_i^L. \tag{19}$$

Considering the term $\hat{Z}\hat{N}^{-1}\hat{L}^{(0)}$ as a perturbation, one obtains in the zeroth order Eq. (20), which is identical to the IORA equation [note that $\hat{L}^{(0)}$ is identical to $\hat{H}^{\mathrm{ZORA}}$ and $\hat{N}$ is defined in Eq. (16)],

$$\hat{L}^{(0)}\psi_i^{(0)} = \epsilon_i^{(0)}\hat{N}\psi_i^{(0)}, \tag{20}$$

where $\psi_i^{(0)}$ denotes the IORA wave function, which approximates the large component ψ_i^L of the Dirac wave function.

By applying standard Rayleigh–Schrödinger perturbation theory[26] to Eq. (19), one obtains Eqs. (21) and (22) for the first- and second-order corrections to $\epsilon_i^{(0)}$,

$$\epsilon_i^{(1)} = \langle \psi_i^{(0)} | \hat{Z}\hat{N}^{-1}\hat{L}^{(0)} | \psi_i^{(0)} \rangle, \tag{21}$$

$$\epsilon_i^{(2)} = \sum_{k \neq i} \frac{\langle \psi_i^{(0)} | \hat{Z}\hat{N}^{-1}\hat{L}^{(0)} | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{Z}\hat{N}^{-1}\hat{L}^{(0)} | \psi_i^{(0)} \rangle}{\epsilon_i^{(0)} - \epsilon_k^{(0)}}. \tag{22}$$

Since the unperturbed wave function $\psi_i^{(0)}$ is normalized on a metric different from that used in standard Rayleigh–Schrödinger perturbation theory,[26] the derivation of Eqs. (21) and (22) is outlined in Appendix B.

V. EVALUATION OF MATRIX ELEMENTS

For the purpose of representing the operator $\hat{Z}$ in matrix form,[27] we introduce a basis of (generally nonorthogonal) functions χ_μ and express the wave functions $\psi_i^{(0)}$ as

$$\psi_i^{(0)} = \sum_\mu \chi_\mu C_{\mu i}^{(0)}, \tag{23}$$

where $C_{\mu i}^{(0)}$ denotes a set of expansion coefficients. Utilizing the new basis, the resolution of the identity is given by[27]

$$\sum_{\mu,\nu} |\chi_\mu\rangle \mathbf{S}_{\mu\nu}^{-1} \langle\chi_\nu| = \hat{I}, \tag{24}$$

where $\mathbf{S}_{\mu\nu}^{-1}$ is an element of the inverse of the overlap matrix $\mathbf{S}$ with elements $\mathbf{S}_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle$. The matrix of the inverse operator $\hat{N}^{-1}$ is given by

$$\langle\chi_\mu|\hat{N}^{-1}|\chi_\mu\rangle = \sum_{\sigma,\tau} \mathbf{S}_{\mu\sigma}\mathbf{N}_{\sigma\tau}^{-1}\mathbf{S}_{\tau\nu}, \tag{25}$$

which follows from the operator identity $\hat{N}^{-1}\hat{N} = \hat{I}$ and where $\mathbf{N}_{\sigma\tau}^{-1}$ denotes an element of the inverse of matrix $\mathbf{N}$ with elements $\mathbf{N}_{\sigma\tau} = \langle\chi_\sigma|\hat{N}|\chi_\tau\rangle$. If one inserts the resolution of the identity between the operators of Eq. (17) and uses Eq. (25), then, for the matrix representation of the operator $\hat{Z}$, Eq. (26) will be obtained,

$$\begin{aligned}
\mathbf{Z} = {}&\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)} - \mathbf{x}_3\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)} + \mathbf{x}_2\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)} + \mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)} + \mathbf{x}_4\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)} \\
&+ \mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)} + \mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)} \\
&+ \mathbf{x}_2\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)} + \mathbf{x}_2\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)} \\
&- \mathbf{x}_2\mathbf{N}^{-1}\mathbf{x}_3\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)} - \mathbf{x}_3\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)} - \mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{x}_3\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)} \\
&- \mathbf{x}_3\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)} - \mathbf{x}_3\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{L}^{(0)}\mathbf{N}^{-1}\mathbf{x}_2\mathbf{N}^{-1}\mathbf{L}^{(0)} + \cdots, \tag{26}
\end{aligned}$$

where $\mathbf{x}_k$ denotes the matrix of the operator $\hat{x}_k$ and $\mathbf{L}^{(0)}$ stands for the matrix of the operator $\hat{L}^{(0)}$.

Equation (20) in matrix representation reads

$$\mathbf{L}^{(0)}\mathbf{C}^{(0)} = \mathbf{N}\mathbf{C}^{(0)}\underline{\underline{\epsilon}}^{(0)}, \tag{27}$$

where $\mathbf{C}^{(0)}$ is the matrix composed from the column vectors of the expansion coefficients $C_{\mu i}^{(0)}$ and $\underline{\underline{\epsilon}}^{(0)}$ is the diagonal matrix of the orbital energies $\epsilon_i^{(0)}$. Just to remind, the matrix $\mathbf{L}^{(0)}$ is identical to the matrix $\mathbf{H}^{\text{ZORA}}$ and we stick to the former notation merely for consistency with other formulas in the current paper. The matrix $\mathbf{C}^{(0)}$ of the IORA orbital coefficients is normalized by the following condition:

$$(\mathbf{C}^{(0)})^\dagger \mathbf{N}\mathbf{C}^{(0)} = \mathbf{I}, \tag{28}$$

where $\mathbf{I}$ is the unity matrix. From Eq. (28), it follows that

$$\mathbf{N}^{-1} = \mathbf{C}^{(0)}(\mathbf{C}^{(0)})^\dagger, \tag{29}$$

where $\mathbf{N}^{-1}$ is the inverse of the matrix $\mathbf{N}$. From Eqs. (27) and (28), it also follows that

$$(\mathbf{C}^{(0)})^\dagger \mathbf{L}^{(0)}\mathbf{C}^{(0)} = \underline{\underline{\epsilon}}^{(0)}. \tag{30}$$

Substituting Eqs. (29) and (30) into Eq. (26) and converting the resulting equation back to the operator notation, one obtains Eq. (31) for the matrix elements of the operator $\hat{Z}\hat{N}^{-1}\hat{L}^{(0)}$,

$$\begin{aligned}
\langle\psi_k^{(0)}|\hat{Z}\hat{N}^{-1}\hat{L}^{(0)}|\psi_i^{(0)}\rangle = {}&\langle\psi_k^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle\epsilon_i^{(0)}\epsilon_i^{(0)} - \langle\psi_k^{(0)}|\hat{x}_3|\psi_i^{(0)}\rangle\epsilon_i^{(0)}\epsilon_i^{(0)}\epsilon_i^{(0)} + \sum_j \langle\psi_k^{(0)}|\hat{x}_2|\psi_j^{(0)}\rangle\langle\psi_j^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle\epsilon_i^{(0)}\epsilon_i^{(0)}\epsilon_i^{(0)} \\
&+ \sum_j \langle\psi_k^{(0)}|\hat{x}_2|\psi_j^{(0)}\rangle\epsilon_j^{(0)}\langle\psi_j^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle\epsilon_i^{(0)}\epsilon_i^{(0)} + \langle\psi_k^{(0)}|\hat{x}_4|\psi_i^{(0)}\rangle\epsilon_i^{(0)}\epsilon_i^{(0)}\epsilon_i^{(0)}\epsilon_i^{(0)} \\
&+ \sum_{j,l} \langle\psi_k^{(0)}|\hat{x}_2|\psi_j^{(0)}\rangle\epsilon_j^{(0)}\langle\psi_j^{(0)}|\hat{x}_2|\psi_l^{(0)}\rangle\epsilon_l^{(0)}\langle\psi_l^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle\epsilon_i^{(0)}\epsilon_i^{(0)} \\
&+ \sum_{j,l} \langle\psi_k^{(0)}|\hat{x}_2|\psi_j^{(0)}\rangle\epsilon_j^{(0)}\langle\psi_j^{(0)}|\hat{x}_2|\psi_l^{(0)}\rangle\langle\psi_l^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle\epsilon_i^{(0)}\epsilon_i^{(0)}\epsilon_i^{(0)}
\end{aligned}$$

$$+ \sum_{j,l} \langle \psi_k^{(0)}|\hat{x}_2|\psi_j^{(0)}\rangle \langle \psi_j^{(0)}|\hat{x}_2|\psi_l^{(0)}\rangle \epsilon_l^{(0)} \langle \psi_l^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle \epsilon_i^{(0)} \epsilon_i^{(0)} \epsilon_i^{(0)}$$

$$+ \sum_{j,l} \langle \psi_k^{(0)}|\hat{x}_2|\psi_j^{(0)}\rangle \langle \psi_j^{(0)}|\hat{x}_2|\psi_l^{(0)}\rangle \epsilon_l^{(0)} \epsilon_l^{(0)} \langle \psi_l^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle \epsilon_i^{(0)} \epsilon_i^{(0)}$$

$$- \sum_{j} \langle \psi_k^{(0)}|\hat{x}_2|\psi_j^{(0)}\rangle \langle \psi_j^{(0)}|\hat{x}_3|\psi_i^{(0)}\rangle \epsilon_i^{(0)} \epsilon_i^{(0)} \epsilon_i^{(0)} \epsilon_i^{(0)} - \sum_{j} \langle \psi_k^{(0)}|\hat{x}_3|\psi_j^{(0)}\rangle \langle \psi_j^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle \epsilon_i^{(0)} \epsilon_i^{(0)} \epsilon_i^{(0)} \epsilon_i^{(0)}$$

$$- \sum_{j} \langle \psi_k^{(0)}|\hat{x}_2|\psi_j^{(0)}\rangle \epsilon_j^{(0)} \langle \psi_j^{(0)}|\hat{x}_3|\psi_i^{(0)}\rangle \epsilon_i^{(0)} \epsilon_i^{(0)} \epsilon_i^{(0)} - \sum_{j} \langle \psi_k^{(0)}|\hat{x}_3|\psi_j^{(0)}\rangle \epsilon_j^{(0)} \langle \psi_j^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle \epsilon_i^{(0)} \epsilon_i^{(0)} \epsilon_i^{(0)}$$

$$- \sum_{j} \langle \psi_k^{(0)}|\hat{x}_3|\psi_j^{(0)}\rangle \epsilon_j^{(0)} \epsilon_j^{(0)} \langle \psi_j^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle \epsilon_i^{(0)} \epsilon_i^{(0)} + \cdots . \tag{31}$$

The next step requires the evaluation of integrals $\langle \psi_i^{(0)}|\hat{x}_k|\psi_j^{(0)}\rangle$. Because the $\hat{x}_k$ operators contain the potential V in the denominator, it may seem that these integrals can be evaluated only by numeric quadratures. However, the use of the resolution of the following identity:

$$(2m)^{-1} \sum_{\mu,\nu} |(\boldsymbol{\sigma}\cdot\mathbf{p})\chi_\mu\rangle \mathbf{T}_{\mu\nu}^{-1} \langle(\boldsymbol{\sigma}\cdot\mathbf{p})\chi_\nu| = \hat{I}, \tag{32}$$

where $\mathbf{T}^{-1}$ is the inverse of the matrix of the nonrelativistic kinetic energy operator $\hat{t}=(\boldsymbol{\sigma}\cdot\mathbf{p})^2/(2m)$, enables one to evaluate the matrix elements of the $\hat{x}_k$ operators analytically. Inserting Eq. (32) between the factors $1/(2mc^2-V)$ in Eq. (15) one arrives at Eq. (33) for the matrix of the operator $\hat{x}_k$,

$$\mathbf{x}_k = (2mc^2)^{-k}\mathbf{K}(\mathbf{T}^{-1}\mathbf{K})^k, \tag{33}$$

where $\mathbf{K}$ is the matrix of the ZORA kinetic energy operator $\hat{K}=(\boldsymbol{\sigma}\cdot\mathbf{p})[c^2/(2mc^2-V)](\boldsymbol{\sigma}\cdot\mathbf{p})$. Using the matrix representation for operators $\hat{x}_k$ one can easily calculate the integrals in Eq. (31) according to

$$\langle \psi_i^{(0)}|\hat{x}_k|\psi_j^{(0)}\rangle = (\mathbf{C}_i^{(0)})^{\dagger}\mathbf{x}_k\mathbf{C}_j^{(0)}$$
$$= (2mc^2)^{-k}(\mathbf{C}_i^{(0)})^{\dagger}\mathbf{K}(\mathbf{T}^{-1}\mathbf{K})^k\mathbf{C}_j^{(0)}. \tag{34}$$

The algorithm for the analytic calculation of the ZORA kinetic energy matrix $\mathbf{K}$ was developed earlier[12,13] and is represented as follows:

$$\mathbf{K} = \mathbf{T} + (\mathbf{W}_0^{-1} - \mathbf{T}^{-1})^{-1}, \tag{35}$$

where $\mathbf{W}_0$ represents the matrix of the operator $(\boldsymbol{\sigma}\cdot\mathbf{p}) \times [V/(4m^2c^2)](\boldsymbol{\sigma}\cdot\mathbf{p})$, which can be easily calculated with the use of the standard nonrelativistic quantum-chemical codes. A somewhat easier way of calculating the matrix $\mathbf{K}$ is based on the fact that for two symmetric matrices $\mathbf{A}$ and $\mathbf{B}$ the following holds:

$$(\mathbf{A}^{-1} - \mathbf{B}^{-1})^{-1} = \mathbf{B}(\mathbf{B}-\mathbf{A})^{-1}\mathbf{B} - \mathbf{B}, \tag{36}$$

which leads to Eq. (37) for the matrix $\mathbf{K}$,

$$\mathbf{K} = \mathbf{T}(\mathbf{T}-\mathbf{W}_0)^{-1}\mathbf{T}. \tag{37}$$

Equation (37) requires that only a single matrix is inverted rather than three as in Eq. (35).

VI. EXPANSION OF THE DIRAC EIGENENERGY IN TERMS OF THE IORA EIGENVALUES

Having developed an algorithm for calculating the matrix elements in Eq. (31), the first- and second-order corrections to the IORA energy as given in Eqs. (21) and (22) can be calculated. Because the expression for the expectation value of the operator $\hat{Z}\hat{N}^{-1}\hat{L}^{(0)}$, Eq. (31), is infinitely long, it should be subjected to certain restrictions. An obvious way to restrict this expression is to use all terms up to the third order in the IORA eigenenergy $\epsilon_i^{(0)}$ [i.e., the first four terms in Eq. (31)] when calculating the first-order correction (21) alone. Indeed, according to Eq. (22), the contributions of the fourth order in $\epsilon_i^{(0)}$ will appear when calculating the correction of the second order in the $\hat{Z}\hat{N}^{-1}\hat{L}^{(0)}$ operator. Thus, there is no need to go beyond the $(\epsilon_i^{(0)})^3$ terms in Eq. (21), if one is interested in the first-order correction only. However, if both first- and second-order corrections are to be calculated, it is consistent to include the $(\epsilon_i^{(0)})^4$ terms into the first-order correction (21). This means that we effectively switch from the expansion of the positive-energy eigenvalues of the Dirac Hamiltonian with respect to the $\hat{Z}\hat{N}^{-1}\hat{L}^{(0)}$ operator to the expansion with respect to the IORA eigenenergy $\epsilon_i^{(0)}$.

Apparently, the resulting perturbational expansion could be designated as IORA(n), where n denotes the order in the IORA eigenenergy $\epsilon_i^{(0)}$. However, this notation has already been used by Dyall and van Lenthe,[8] who developed a somewhat different perturbational expansion of the Dirac eigenergy. Their work[8] is based on the assumption that the exact solution to the Dirac equation is known, which leads to the energy-dependent algebraic expression for the operator $\hat{X}$ in the following:

$$\mathbf{X} = \frac{c}{2mc^2 - V + \epsilon_i}(\boldsymbol{\sigma}\cdot\mathbf{p}). \tag{38}$$

Equation (38) is consistent with Eq. (3) as long as the operator $\hat{X}$ acts on the large component ψ_i^L of the Dirac eigenfunction, but is not valid otherwise. Note that in the present work no reference to the exact solution of the Dirac equation was made. The present derivation follows directly from the algebraic form of the non-Hermitian operator $\hat{L}$ and does not rely

TABLE I. Ground state energies (in hartree) for hydrogen-like atomic ions with varying nuclear charge. All calculations employ the basis set of 50 Gaussian-type functions taken from Ref. 28.

Method	20[a]	40	60	80	100	120	92
Dirac eq.[b]	−201.076 523	−817.807 498	−1895.682 36	−3532.192 15	−5939.1954	−9 710.7835	−4861.1980
IORA[c]	−201.082 194	−818.171 958	−1899.900 01	−3556.901 02	−6042.5850	−10 089.4142	−4921.0993
IORA3[c,d]	−201.076 516	−817.806 523	−1895.673 09	−3532.206 01	−5939.5728	−9 712.0963	−4861.3512
IORA4[c,e]	−201.076 521	−817.807 407	−1895.680 67	−3532.193 70	−5939.3800	−9 712.8699	−4861.2527
IORA3(2)[c,f]	−201.076 522	−817.807 487	−1895.681 96	−3532.181 79	−5939.0659	−9 709.7282	−4861.1475
SIORA3/2[c,g]	−201.076 522	−817.807 654	−1895.684 33	−3532.192 20	−5939.1129	−9 710.3178	−4861.1699
IORA(3)[h]							−4859.9034
TIORA[h]							−4861.1475
DKH2[i]	−201.072 538	−817.615 772	−1893.897 64	−3523.324 84	−5906.1918	−9 594.0960	
DKH3[i]	−201.076 660	−817.820 110	−1895.844 04	−3533.119 56	−5942.3694	−9 712.9311	
DKH5[i]	−201.076 523	−817.808 095	−1895.702 82	−3532.461 47	−5941.5285	−9 730.9684	
DPT(1)[j]					−5665.6420		
DPT(2)[j]					−5842.8737		
DPT(8)[j]					−5938.5990		
DPT(10)[j]					−5939.0651		
DPT(11)[j]					−5939.1336		

[a]Nuclear charge.
[b]Analytic results from the Dirac equation.
[c]Calculated in this work with the basis set of 50 primitive Gaussian functions from Ref. 28.
[d]Equation (39) in this work.
[e]Equation (40) in this work.
[f]Equation (45) in this work.
[g]Equation (47) in this work.
[h]Numeric results from Ref. 8.
[i]From Ref. 28. DKHn stands for the Douglas–Kroll–Hess method of nth order.
[j]Analytic results from Ref. 29. DPT(n) stands for the direct perturbation theory accurate through $1/c^{2n}$.

on Eq. (38). For the purpose of making a distinction between the present work and the earlier work of Dyall and van Lenthe,[8] the alternative notation IORAn is used to denote the nth order expansion of the Dirac eigenenergy in terms of the IORA eigenenergies.

Thus, the IORA3 energy is given in the following:

$$\epsilon_i^{\text{IORA3}} = \epsilon_i^{(0)} + \langle \psi_i^{(0)} | \hat{x}_2 | \psi_i^{(0)} \rangle \epsilon_i^{(0)} \epsilon_i^{(0)}$$

$$- \langle \psi_i^{(0)} | \hat{x}_3 | \psi_i^{(0)} \rangle \epsilon_i^{(0)} \epsilon_i^{(0)} \epsilon_i^{(0)}$$

$$+ \sum_j \langle \psi_i^{(0)} | \hat{x}_2 | \psi_j^{(0)} \rangle \langle \psi_j^{(0)} | \hat{x}_2 | \psi_i^{(0)} \rangle \epsilon_i^{(0)} \epsilon_i^{(0)} \epsilon_i^{(0)}$$

$$+ \sum_j \langle \psi_i^{(0)} | \hat{x}_2 | \psi_j^{(0)} \rangle \epsilon_j^{(0)} \langle \psi_j^{(0)} | \hat{x}_2 | \psi_i^{(0)} \rangle \epsilon_i^{(0)} \epsilon_i^{(0)}.$$

$$(39)$$

Along with these terms, the IORA4 energy, Eq. (40), includes the $(\epsilon_i^{(0)})^4$ terms into the first-order correction (21) [see Eq. (31)—note that the index k now must be replaced with i] and the contribution of the fourth order in $\epsilon_i^{(0)}$ from Eq. (22),

$$\epsilon_i^{\text{IORA4}} = \epsilon_i^{\text{IORA3}} + \{\text{fourth-order terms from Eq. (31)}\}$$

$$+ \sum_{k \neq i} \frac{\langle \psi_i^{(0)} | \hat{x}_2 | \psi_k^{(0)} \rangle \epsilon_k^{(0)} \epsilon_k^{(0)} \langle \psi_k^{(0)} | \hat{x}_2 | \psi_i^{(0)} \rangle}{\epsilon_i^{(0)} - \epsilon_k^{(0)}} \epsilon_i^{(0)} \epsilon_i^{(0)}.$$

$$(40)$$

Numeric accuracy of these approximations is tested in the calculation of the ground state energy of a number of hydrogen-like atomic ions presented in Table I. In these calculations, the basis set of 50 primitive s-type Gaussian functions taken from work of Wolf et al.[28] is employed. Since we are interested in the ground states of one-electron atoms, for which the spin–orbit interaction does not play any role, the latter was neglected in the calculations. The results of the present work are compared in Table I with the results of other investigations reported in the literature.

In general, for all hydrogen-like ions considered, the IORA3 and IORA4 approximations show fast convergence to the Dirac energy and are superior to the Douglas–Kroll–Hess (DKH) method[28,30,31] up to the fifth order (the highest order of the DKH theory reported in the literature). This is especially pronounced for ions with high Z. The last five lines in Table I list the results from a direct perturbation theory (DPT)[29,32] calculation of the hydrogen-like fermium (Z=100) taken from the work of Rutkowski et al.[29] The comparison reveals that the IORA3 and IORA4 approximations achieve the same or even better accuracy as the DPT(8) calculation exact through $1c^{-16}$. The only difference with DPT is that the latter converges to the exact Dirac eigenvalue from above, whereas the IORAn approximations converge from below.

A separate entry was made for hydrogen-like uranium ion for the purpose of a comparison with the earlier work of Dyall and van Lenthe,[8] who used the alternative approach to a perturbational improvement of the IORA eigenenergy. The IORA3 approximation, which is analogous to the IORA(3) method reported by Dyall and van Lenthe,[8] is clearly supe-

rior to the latter. However, it does not reach the accuracy of the so-called TIORA method,[8] which is approximately correct to third order in $\epsilon_i^{(0)} = \epsilon_i^{IORA}$ and combines the IORA(3) energy with certain contributions from the fourth-order IORA(4) approximation. Although TIORA is only an approximation within the Dyall and van Lenthe approach,[8] it will be shown in the following that this method follows naturally from an alternative formulation of relativistic perturbation theory based on the effective Hamiltonian $\hat{L}$, Eq. (17).

VII. DOUBLE PERTURBATION THEORY WITH AN EFFECTIVE HERMITIAN HAMILTONIAN

The operator $\hat{L}$ obtained with the help of similarity transformation (5) is non-Hermitian. Using Eqs. (4), (7), and (8), it is possible to show[21] that the large component ψ_i^L of the Dirac wave function ψ_i^D satisfies

$$\tfrac{1}{2}[(1+\hat{X}^\dagger\hat{X})\hat{L}+\hat{L}^\dagger(1+\hat{X}^\dagger\hat{X})]\psi_i^L = \epsilon_i(1+\hat{X}^\dagger\hat{X})\psi_i^L. \tag{41}$$

In Eq. (41), the operator in square brackets on the left-hand side is Hermitian. However, the transformation to a Hermitian form comes at the price of an explicit dependence on the relativistic normalization operator $1+\hat{X}^\dagger\hat{X}$. Contrary to the linear operator $\hat{L}$, this operator is quadratic in $\hat{X}$ and, consequently, it has a more complicated structure than $\hat{L}$. However, up to terms quadratic in $\hat{L}^{(0)}$, the algebraic expression for this operator is still simple,

$$1+\hat{X}^\dagger\hat{X} = 1+(\hat{X}^{(0)})^\dagger\hat{X}^{(0)} - \hat{x}_2\hat{N}^{-1}\hat{L}^{(0)} - \hat{L}^{(0)}\hat{N}^{-1}\hat{x}_2$$
$$+\hat{L}^{(0)}\hat{N}^{-1}\hat{x}_3\hat{N}^{-1}\hat{L}^{(0)}+\cdots. \tag{42}$$

Because our primary goal is to expand the exact relativistic energy ϵ_i in terms of the IORA eigenenergies $\epsilon_i^{(0)}$, Eq. (42) can be used for the expansion correct at least through third order in $\epsilon_i^{(0)}$.

We rewrite the operators in Eq. (41) according to

$$\hat{L} = \hat{N}^{-1}(\hat{L}^{(0)}+\hat{Z}\hat{N}^{-1}\hat{L}^{(0)}) = \hat{N}^{-1}(\hat{L}^{(0)}+\hat{L}^{(1)}), \tag{43a}$$

$$1+\hat{X}^\dagger\hat{X} = \hat{N}+\hat{N}^{(1)}, \tag{43b}$$

where $\hat{N} = 1+(\hat{X}^{(0)})^\dagger\hat{X}^{(0)}$ is the IORA normalization operator [see Eq. (16)] and the operator $\hat{Z}$ is defined in Eq. (18), Furthermore, we consider $\hat{N}^{(1)}$ and $\hat{L}^{(1)}$ as perturbations to the normalization operator of the wave function and to the Hamiltonian, respectively. Then, in the zeroth order of double perturbation theory (see Appendix C), the IORA equation (20) emerges. The correction to the IORA energy, which combines linear and bilinear terms in the perturbation expansion, is given in Eq. (C11). The reason why the bilinear term $\epsilon_i^{(11)}$, Eq. (C8), is included is that it contains the contributions of the third order in $\epsilon_i^{(0)}$. The higher-order corrections such as $\epsilon_i^{(20)}$, $\epsilon_i^{(02)}$, etc., depend on the perturbed wave function and, as is obvious from Eq. (C13), make contributions of at least fourth order in $\epsilon_i^{(0)}$. The same is true for the last two terms in Eq. (C11) [see also Eq. (C14)]. Thus, these terms can be neglected in the derivation of a third-order energy correction.

Using Eq. (29) for the operator $\hat{N}^{-1}$, Eq. (C11) (with the last two terms omitted) can be rewritten as in the following:

$$\epsilon_i^{IORA3(2)} = \epsilon_i^{(0)} + \tfrac{1}{2}\langle\psi_i^{(0)}|\hat{L}^{(1)}+(\hat{L}^{(1)})^\dagger|\psi_i^{(0)}\rangle$$

$$+ \tfrac{1}{2}\sum_{k\neq i}\langle\psi_i^{(0)}|\hat{N}^{(1)}|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|\hat{L}^{(1)}|\psi_i^{(0)}\rangle$$

$$+ \tfrac{1}{2}\sum_{k\neq i}\langle\psi_i^{(0)}|(\hat{L}^{(1)})^\dagger|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|\hat{N}^{(1)}|\psi_i^{(0)}\rangle, \tag{44}$$

where the notation IORA$n(2)$ means that the energy correct through nth order in $\epsilon_i^{(0)}$ is obtained from double perturbation theory. For consistency with previous derivations, $\psi_i^{(00)}$ and $\epsilon_i^{(00)}$ are replaced by $\psi_i^{(0)}$ and $\epsilon_i^{(0)}$. Note, that the zeroth-order wave function and energy are identical in both perturbation theories, i.e., $\psi_i^{(00)} \equiv \psi_i^{(0)}$ and $\epsilon_i^{(00)} \equiv \epsilon_i^{(0)}$. The sum of the first two terms on the right-hand side of Eq. (44) is exactly equivalent to the IORA3 energy. As for the last two terms in Eq. (44), only the contributions into $\hat{L}^{(1)}$, which are quadratic in $\hat{L}^{(0)}$, i.e., the second term on the right-hand side of Eq. (17), and the contributions into $\hat{N}^{(1)}$, which are linear in $\hat{L}^{(0)}$, i.e., the third and fourth terms on the right-hand side of Eq. (42), should be used. Upon substituting them into Eq. (44) one obtains

$$\epsilon_i^{IORA3(2)}$$

$$= \epsilon_i^{IORA3} - \sum_{k\neq i}\langle\psi_i^{(0)}|\hat{x}_2|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle\epsilon_i^{(0)}\epsilon_i^{(0)}\epsilon_i^{(0)}$$

$$- \sum_{k\neq i}\langle\psi_i^{(0)}|\hat{x}_2|\psi_k^{(0)}\rangle\epsilon_k^{(0)}\langle\psi_k^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle\epsilon_i^{(0)}\epsilon_i^{(0)}$$

$$= \epsilon_i^{(0)} + \langle\psi_i^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle\epsilon_i^{(0)}\epsilon_i^{(0)}$$

$$- \langle\psi_i^{(0)}|\hat{x}_3|\psi_i^{(0)}\rangle\epsilon_i^{(0)}\epsilon_i^{(0)}\epsilon_i^{(0)}$$

$$+ 2\langle\psi_i^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|\hat{x}_2|\psi_i^{(0)}\rangle\epsilon_i^{(0)}\epsilon_i^{(0)}\epsilon_i^{(0)}, \tag{45}$$

which is exactly equivalent to the TIORA energy defined in Eq. (45) of Ref. 8. Note, that the $\hat{x}_k$ operators defined in Eq. (15) are connected with the $\hat{G}_k$ operators used by Dyall and van Lenthe:[8]

$$\hat{x}_k = \frac{\hat{G}_k}{(2mc^2)^k}. \tag{46}$$

Thus, with the use of double perturbation theory the equivalence between the IORA3(2) and the TIORA approaches is demonstrated. TIORA is not a method approximately correct to third order in $\epsilon_i^{(0)}$, as was originally claimed,[8] but is the exact third-order method when corrections to both the relativistic wave function metric and the relativistic Hamiltonian are incorporated.

The results of the IORA3(2) calculations for hydrogen-like atomic ions are presented in Table I. Although IORA3(2) is formally correct only to order $(\epsilon_i^{(0)}/(2mc^2))^3$, this method yields results of a considerably higher accuracy than could have been expected for a method correct to c^{-6}. In fact, the IORA3(2) results are as accurate as the DPT(10) results, i.e., a method correct to order c^{-20}.

VIII. SCALED IORA METHOD

Although it seems tempting to use Eq. (41) together with the expressions for the operators $\hat{L}$, Eq. (17), and $1 + \hat{X}^\dagger \hat{X}$, Eq. (42), in variational calculations, a caveat against such an idea is appropriate. Indeed, the expressions for these operators result from a sign-alternating series in $\hat{L}^{(0)}$. Because the matrix elements of the operators $\hat{x}_k$ are inversely proportional to $(2mc^2)^{-k}$ [see Eq. (46)], these series will converge if all eigenvalues of the $\hat{L}^{(0)}$ Hamiltonian are in absolute magnitude smaller than $2mc^2$. For a Coulomb potential (with $Z < c$), the effective Hamiltonian $\hat{L}^{(0)}$ does not possess bound eigenvalues lower than $-2mc^2$. However, it may possess unbound eigenvalues larger than $2mc^2$. For these high-lying unbound energy levels, the truncated expressions, such as Eqs. (17) and (42), are divergent and yield meaningless results. For instance, when trying to solve Eq. (41) with the truncated operators $\hat{L}$ and $1 + \hat{X}^\dagger \hat{X}$ variationally, spurious roots much lower than $-2mc^2$ are obtained, which indicates a variational collapse. These roots can be eliminated and reasonable energies can be obtained, if all positive IORA eigenvalues larger than $2mc^2$ are omitted, when calculating the matrix elements of the $\hat{L}$ and $1 + \hat{X}^\dagger \hat{X}$ operators. Evidently, this is not convenient for practical calculations with Eq. (41).

For states in the energy interval $[-2mc^2, 2mc^2]$, the use of the truncated expressions does not pose any danger and the improved energy values can be obtained from the Rayleigh quotient (47) with the IORA wave function,

$$\epsilon_i^{\text{SIORA}n/m} = \frac{\frac{1}{2} \langle \psi_i^{(0)} | (1 + \hat{X}^\dagger \hat{X}) \hat{L} + \hat{L}^\dagger (1 + \hat{X}^\dagger \hat{X}) | \psi_i^{(0)} \rangle}{\langle \psi_i^{(0)} | 1 + \hat{X}^\dagger \hat{X} | \psi_i^{(0)} \rangle}. \tag{47}$$

Note that minimization of this quotient with respect to the wave function leads to the exact relativistic equation (41).

The name *scaled IORA* (SIORA) is suggested for this approach, because it is based on the use of the Rayleigh quotient with an approximate wave function, which is similar to what was done in the scaled ZORA method.[2] However, the scaled ZORA method uses the Rayleigh quotient obtained from the IORA equation (20),[8] which does not lead to the exact relativistic equation upon variation of the trial wave function. The SIORA method, on the contrary, employs the Rayleigh quotient which leads to the exact relativistic equation for the large-component wave function, Eq. (41).

Since the operators $\hat{L}$ and $1 + \hat{X}^\dagger \hat{X}$ are obtained from a truncated expansion valid through a finite order in $\hat{L}^{(0)}$, two additional indices n and m are used to designate the scaled IORA method: the first indicates that the effective Hamiltonian $\hat{L}$ is correct to nth order and the second belongs to the normalization operator $1 + \hat{X}^\dagger \hat{X}$. Combination of the third-order expression for $\hat{L}$ with Eq. (42) furnishes the SIORA3/2 method. This method is computationally as simple as IORA3(2) (or TIORA), however it leads to somewhat more accurate results, especially for heavy atoms (see Table I). Whereas IORA3(2) produces for hydrogen-like fermium ($Z = 100$) results of the same quality as DPT(10), the

SIORA3/2 value is closer to the DPT(11), i.e., the energy is accurate to c^{-22}.

Although the scaled ZORA method yields for a one-electron atom exactly the Dirac eigenvalues,[2] it employs the ZORA wave function, which is quite inaccurate for the lowest atomic energy levels.[2,7,8] The SIORA method uses the IORA wave function, which is much more accurate, especially in the core regions of atoms.[8] For instance, the relative absolute error in the expectation values of the operators $\mathbf{r}^n$ calculated with the ZORA wave function for the hydrogen-like uranium ion reaches 12% for $\mathbf{r}$ and more than 40% for $\mathbf{r}^{-2}$.[8] With the use of the IORA wave function, the error is reduced to just 3% in the case of the $\langle \mathbf{r}^{-2} \rangle$ value for the $1s$ orbital of U^{91+}.[8] As for the orbital radii $\langle \mathbf{r} \rangle$, the relative error for the $1s$ orbital of U^{91+} is only 1.3%,[8] which is comparable to the errors obtained in the DKH2 calculation for the much lighter bromine.[31] For other orbitals, the relative errors are in the range of 0.01% and less.[8] Thus, the SIORA method combines a very accurate quasirelativistic wave function with the improved energy estimate.

For practical purposes, the SIORA equation can be written in exactly the same algebraic form as the IORA equation (20), however, following the Hamiltonian:

$$\hat{H}^{\text{SIORA}n/m} = \sum_k^{\epsilon_k^{(0)} < 2mc^2} |\psi_k^{(0)}\rangle \epsilon_k^{\text{SIORA}n/m} \langle \psi_k^{(0)}| $$
$$+ \sum_k^{\epsilon_k^{(0)} \geqslant 2mc^2} |\psi_k^{(0)}\rangle \epsilon_k^{(0)} \langle \psi_k^{(0)}|, \tag{48}$$

where the summation with respect to the IORA eigenstates is split into two intervals $\epsilon_k^{(0)} < 2mc^2$ and $\epsilon_k^{(0)} \geqslant 2mc^2$ for the reason described at the beginning of this section. Obviously, Eq. (20) with the Hamiltonian (48) yields the IORA eigenfunctions $\psi_i^{(0)}$ and the SIORAn/m eigenenergies. In matrix form, Eq. (48) transforms to

$$\mathbf{H}^{\text{SIORA}n/m} = \mathbf{N}\mathbf{C}^{(0)} \underline{\underline{\zeta}} \, \underline{\underline{\epsilon}}^{(0)} (\mathbf{C}^{(0)})^\dagger \mathbf{N}, \tag{49}$$

where $\underline{\zeta}$ is the diagonal matrix of the scaling coefficients defined in the following:

$$\zeta_k = \begin{cases} \epsilon_k^{\text{SIORA}n/m} / \epsilon_k^{(0)}, & \epsilon_k^{(0)} < 2mc^2 \\ 1, & \epsilon_k^{(0)} \geqslant 2mc^2. \end{cases} \tag{50}$$

IX. IMPLEMENTATION OF IORA*n* AND SIORA*n/m*

The formalism developed in the previous sections applies to one-electron systems. In case of many-electron systems, the electron–electron repulsion potential should be included into the Dirac equation. Even in the simplest case of pure Coulomb repulsion $1/r_{ij}$, which is not Lorentz-invariant, the subsequent transformations of the Dirac Hamiltonian, which lead to the effective Hamiltonian $\hat{L}$, become very complicated. However, if one assumes that the electron–electron repulsion operator commutes with the operator $\hat{X}$, Eqs. (3) and (4), then this operator will become independent of the electron–electron repulsion potential [see Eq. (3)] and the relativistic transformations will include only the electron-nuclear attraction potential. This assumption,

TABLE II. Orbital energies for the xenon atom. Calculations employ the uncontracted relativistic basis set from Ref. 36.

Orbital	Dirac–Fock[a]	ZORA[b]	Scaled ZORA[a]	IORA[b]	SIORA3/2[b]
$1s$	−1277.2511	−1338.8489	−1275.5423	−1278.8691	−1276.6454
$2s$	−202.4603	−205.6187	−202.2547	−202.4880	−202.4516
$2p$	−181.6912	−184.1154	−181.5901	−181.5652	−181.5313
$3s$	−43.0057	−43.4147	−42.9673	−43.0148	−43.0119
$3p$	−36.0988	−36.3625	−36.0811	−36.0818	−36.0790
$3d$	−25.7266	−25.8598	−25.7232	−25.7330	−25.7306
$4s$	−8.4255	−8.4889	−8.4185	−8.4283	−8.4279
$4p$	−6.1350	−6.1644	−6.1320	−6.1321	−6.1318
$4d$	−2.6604	−2.6608	−2.6608	−2.6613	−2.6610
$5s$	−1.0070	−1.0129	−1.0061	−1.0073	−1.0072
$5p$	−0.4541	−0.4544	−0.4537	−0.4535	−0.4534

[a]Taken from Ref. 9.
[b]This work.

known under the name of the one-electron ($1\bar{e}$) approximation,[33] is used in many quasirelativistic computational schemes.[12–16,19,28,31,33] In comparison with the exact formalism, the $1\bar{e}$ approximation neglects terms which include the commutator $[1/r_{ij}, \hat{X}]$, i.e., terms of the same order of magnitude as the electron–electron spin–orbit interaction.[33] As it has been demonstrated in many investigations that[33–35] the neglect of these terms leads to small errors in the total energy, which do not have any chemical significance.

In our previous studies,[12–16] we have applied the $1\bar{e}$ approximation to the IORA and the IORA with modified metric (IORAmm) methods and details of the implementation can be found there. The major advantage of the $1\bar{e}$ approximation is that it can be easily installed in any existing nonrelativistic quantum-chemical program. Within the $1\bar{e}$ approximation, the nonrelativistic one-electron Hamiltonian should be replaced by the quasirelativistic one-electron Hamiltonian, which is renormalized on the nonrelativistic (unit) metric. The renormalization is simple and straightforward. Because the IORA wave function is normalized with respect to the operator $\hat{N}$, the renormalization of the one-electron Hamiltonian is achieved by

$$^{\text{ren}}\hat{H}_{1\bar{e}}^{\text{SIORA}n/m} = \hat{N}^{-1/2} \hat{H}_{1\bar{e}}^{\text{SIORA}n/m} \hat{N}^{-1/2}, \tag{51}$$

where $\hat{H}_{1\bar{e}}^{\text{SIORA}n/m}$ is the SIORA Hamiltonian in the $1\bar{e}$ approximation. In matrix form, Eq. (51) translates to

$$^{\text{ren}}\mathbf{H}_{1\bar{e}}^{\text{SIORA}n/m} = \mathbf{S}^{1/2} \mathbf{N}^{-1/2} \mathbf{H}_{1\bar{e}}^{\text{SIORA}n/m} \mathbf{N}^{-1/2} \mathbf{S}^{1/2}, \tag{52}$$

where $\mathbf{S}$ is the overlap matrix. In order to construct the $\mathbf{H}_{1\bar{e}}^{\text{SIORA}n/m}$ matrix, one needs first to solve the one-electron (matrix) IORA equation (27) with the Hamiltonian $\mathbf{L}^{(0)}$ which includes the electron-nuclear attraction potential V_n only, i.e.,

$$\mathbf{L}^{(0)} = \mathbf{V}_n + \mathbf{T}(\mathbf{T} - \mathbf{W}_0)^{-1} \mathbf{T}, \tag{53}$$

where $\mathbf{V}_n$ is the matrix of the electron-nuclear attraction integrals and the matrix $\mathbf{W}_0$ is calculated using the electron-nuclear attraction potential V_n. In the present work, the spin-dependent relativistic effects are neglected and only the scalar-relativistic (spin-independent) effects are taken explic-

itly into account. This is achieved by replacing the ($\boldsymbol{\sigma} \cdot \mathbf{p}$) operator with the linear momentum operator $\mathbf{p}$ only, when calculating the matrix elements of $\mathbf{W}_0$,

$$(\mathbf{W}_0)_{\mu\nu} = \frac{1}{4m^2c^2} \langle \chi_\mu | \mathbf{p} V_n \cdot \mathbf{p} | \chi_\nu \rangle. \tag{54}$$

Thus, to construct the $^{\text{ren}}\mathbf{H}_{1\bar{e}}^{\text{SIORA}n/m}$ Hamiltonian one needs first to solve Eq. (27) with the Hamiltonian (53), which is achieved by a simple diagonalization. Having obtained the eigenvectors $\mathbf{C}^{(0)}$ and the eigenvalues $\boldsymbol{\epsilon}^{(0)}$, one constructs the renormalized SIORAn/m Hamiltonian according to

$$^{\text{ren}}\mathbf{H}_{1\bar{e}}^{\text{SIORA}n/m} = \mathbf{S}^{1/2} \mathbf{N}^{1/2} \mathbf{C}^{(0)} \underline{\zeta} \underline{\boldsymbol{\epsilon}}^{(0)} (\mathbf{C}^{(0)})^\dagger \mathbf{N}^{1/2} \mathbf{S}^{1/2}, \tag{55}$$

where the scaling factors ζ are given in Eq. (50) for the SIORA3/2 method. The renormalized SIORA Hamiltonian then replaces the one-electron Hamiltonian of the nonrelativistic Hartree–Fock method. Because the modification concerns only the one-electron Hamiltonian, the same programs, which are designed for nonrelativistic correlated calculations, can be used for quasirelativistic SIORA calculations at the correlated level.

The IORAn ($n=2,3,4$), IORA$n(m)$ ($n=2,3,4$, $m=2$), and SIORAn/m ($n=2,3$, $m=1,2$) methods were programmed and implemented into the COLOGNE 2003 suite of quantum-chemical programs.[36] The implementation requires only the modification of the one-electron Hamiltonian, which has been described in the current section.

X. RESULTS AND DISCUSSION

The application of IORAn and IORA$n(2)$ to one-electron atomic ions has already been described in the previous sections and is not repeated here. In the following the focus will be predominantly on SIORA3/2 because this method provides the best results for one-electron ions. SIORA3/2 is applied in *ab initio* calculations on many-electron atoms and molecules using both Hartree–Fock and second-order Møller–Plesset perturbation theory.

A. Atomic calculations

Table II lists the orbital energies for the xenon atom calculated in this work with the ZORA, IORA, and SIORA3/2 methods as well as the results of the Dirac–Fock and scaled ZORA calculations performed by Faas *et al.*[9] All calculations reported in Table II employed the uncontracted $(19s15p9d)$ relativistic basis set developed by Dyall.[37] Although xenon is a relatively light element $(Z=54)$, the relativistic effects on the orbital energies are significant: ~50 hartree for the $1s$ orbital and ~0.06 hartree for the $5s$ orbital.[9] This element was chosen for an analysis of the performance of the methods developed in this work because results of the Dirac–Fock and some quasirelativistic calculations on Xe performed with a well-specified basis set are available in the literature. This facilitates significantly the comparison of the results obtained in the present work with the results of other quasirelativistic investigations.

The ZORA and IORA methods exaggerate the relativistic effects on the orbital energies, where this feature is well-documented in the literature.[1,2,7–13] The SIORA orbital energies are in very good agreement with the Dirac–Fock values. Although for one-electron atoms the scaled ZORA method yields exact energies,[2,3] for a many-electron atom such as xenon, this method is inferior to SIORA. This is a clear manifestation of the improved quality of the IORA wave function as compared to the ZORA one. Better description of the electron density achieved with the use of the IORA wave function results in a better description of the electron–electron interaction. This is especially pronounced in the deep core region, where the SIORA3/2 method reduces more than twice the error made by scaled ZORA.

B. Gauge dependence

In the molecular calculations, an important disadvantage of the IORA and other methods based on the regular approximation (ZORA, etc.) is the erroneous gauge dependence of the energy eigenvalues.[2,8,12,13] If a constant shift is added to the potential V, then the eigenvalues of the Hamiltonian should be shifted by exactly the same amount of energy. This feature is known as the *gauge invariance* and it means merely that it is the difference of potentials rather than the potential itself, which counts in physical events.

The gauge shift error (GSE) of ZORA is of the order of $E/(2mc^2)$,[2,8] i.e., when the potential is shifted by an amount Δ, the shift in the ZORA energy exceeds Δ by a small but non-negligible amount. The gauge shift Δ plays an important role in molecular calculations for the core electrons, because, for a given nucleus, they experience the tails of the potentials of the neighboring nuclei, which means a shift in the potential seen by these electrons by Δ. The closer the nuclei are brought together, the larger is the shift generated by other nuclei at the position of the given nucleus. Because of the gauge noninvariance, the ZORA energy decreases faster than it should, which results in the appearance of nonphysical (attractive) forces between nuclei and in a distortion of the molecular geometry. Although the IORA method has considerably weaker gauge dependence, of the order of

TABLE III. Gauge shift error $E_0^{\text{method}} - E_\Delta^{\text{method}} + \Delta$ (in hartree units) in the ground state energy of noble gas atoms for different methods. The gauge shift Δ is chosen such that the total nonrelativistic energy is shifted by exactly -100 hartrees. Calculations employ the TZV basis set of Ahlrichs and May (Ref. 38) unless noted otherwise.

Atom	ZORA[a]	Scaled ZORA[b]	IORA[a]	SIORA3/2[a]
He	0.003 803	0.000 000 5	0.000 006	−0.000 002
Ne	0.034 280	0.000 016	0.000 084	−0.000 010
Ar	0.077 076	−0.000 18	0.000 464	−0.000 010
Kr	0.199 988	−0.001 8	0.003 781	−0.000 107
Xe	0.375 149[c]	−0.006	0.014 135[c]	−0.000 479[c]

[a]This work.
[b]Taken from Ref. 11.
[c]Calculations employ the uncontracted relativistic basis set from Ref. 37.

$(E/(2mc^2))^2$,[8] for heavy nuclei the GSE still can reach considerable values.[12,13]

The use of the scaled IORA formalism reduces greatly the gauge dependence of the IORA method making the GSE proportional to $(E/(2mc^2))^4$. This is illustrated in Table III, where the results of calculations of the gauge shift error $E_0 - E_\Delta + \Delta$ performed with various methods for noble gas atoms He through Xe are displayed. The negative constant Δ, added to the nuclear potential, is chosen in such a way that the nonrelativistic total atomic energy is shifted by -100 hartree units. The SIORA3/2 method causes a GSE, which is almost two orders of magnitude smaller than that of the IORA method. Although for a one-electron atom the scaled ZORA method is gauge invariant (i.e., zero GSE),[2,3] for many-electron atoms this method is not gauge-invariant[11] and leads to errors almost an order of magnitude larger than SIORA3/2.

C. Molecular calculations

The results of calculations of diatomic, the gold atom containing molecules, AuH, AuF, and Au_2 are collected in Table IV. The calculations employed the contracted $[14s10p9d3f]$ basis set on gold used in our earlier work,[13] and the augmented correlation consistent double-zeta basis set of Dunning (aug-cc-pVDZ)[39] for the light elements. The calculations were carried out at the Hartree–Fock level and at the level of the second-order Møller–Plesset (MP2) perturbation theory.[40] In the MP2 calculations, all valence electrons of light atoms and the $5s$, $4f$, $5p$, $5d$, and $6s$ electrons (33 electrons in total) of the gold atom were correlated. The optimized molecular geometries and the harmonic vibrational frequencies are obtained numerically. No correction for the gauge dependence was made during the geometry optimization. However, the dissociation energies are corrected for gauge noninvariance, by subtracting the GSE for individual atoms from the total molecular energy.[12,13]

Comparison of the results of IORA and SIORA3/2 calculations with the available theoretical and experimental data shows that the IORA method clearly suffers from the gauge dependence problem. Since no correction for the gauge dependence was used during the geometry optimization, the bond lengths obtained with IORA are markedly shorter than the reference values. However, as long as this distortion remains modest, the dissociation energy, which is corrected for

TABLE IV. Spectroscopic parameters of gold diatomic molecules.

Method	R_e (Å)	ω_e (cm^{-1})	D_e (eV)
AuH			
IORA/SCF	1.553	2178	1.76
SIORA3/2/SCF	1.566	2131	1.76
DHF[a]	1.570	2067	1.78
IORA/MP2	1.476	2597	3.24
SIORA3/2/MP2	1.485	2568	3.24
DHF/MP2[a]	1.485	2504	3.21
Expt.[b]	1.524	2305	3.36
AuF			
IORA/SCF	1.918	597	1.09
SIORA3/2/SCF	1.978	522	1.11
DHF[c]	1.968	528	
IORA/MP2	1.856	655	3.24
SIORA3/2/MP2	1.908	589	3.26
DHF/MP2[c]	1.899	590	
Expt.	1.918[d]	560[e]	3.20[f]
Au$_2$			
IORA/SCF	2.070	513	−3.27
SIORA3/2/SCF	2.655	148	0.83
IORA/MP2	2.015	473	−0.33
SIORA3/2/MP2	2.490	184	2.52
Expt.[b]	2.472	191	2.29

[a]Taken from Ref. 41.
[b]Experimental data taken from Ref. 42 unless noted otherwise.
[c]Taken from Ref. 43.
[d]Taken from Ref. 44.
[e]Taken from Ref. 45.
[f]Taken from Ref. 46.

GSE, is reasonable. For the gold dimer, the IORA method predicts an unrealistic geometry with the bond length being almost half of an angstrom shorter than the experimental value. As a consequence of this distortion, the GSE calculated at this geometry is so large that it exceeds the binding energy, thus yielding the negative values for D_e (see Table IV).

For all molecules in Table IV, the SIORA3/2 method leads to results in very good agreement with the reference theoretical and experimental data. The weak gauge dependence does not have a visible effect on the optimized molecular geometries and the vibrational frequencies. Even for the gold dimer, the Au–Au bond length of 2.490 Å, obtained in the SIORA3/2/MP2 calculation, is in excellent agreement with the experimental value of 2.472 Å.

XI. CONCLUSIONS

The following conclusions can be drawn from the present work:

(i) The exact relativistic Hamiltonian for electronic (positive-energy) states was expanded in terms of linear energy-independent operators. The advantage of the regular Hamiltonian operator $\hat{L}^{(0)} = \hat{H}^{ZORA}$ and the operators $\hat{N}$ and $\hat{x}_k$ used in expansion (17) is that they are bound from below and do not contain the singularities typical for the operators obtained in the standard $1/c^2$ expansion, even in the case of a singular potential such as the potential of a point-charge

nucleus. Thus, the expansion obtained can be considered as the regular expansion for the effective relativistic Hamiltonian.

In previous development work, Chang et al.[19] derived the effective Hamiltonian in the recursive form $\hat{H}^{eff} = f(\hat{H}^{eff})$, which is suitable for an iterative numeric solution. Such an approach is not well suited for an implementation within standard quantum-chemical codes. Indeed, the calculation of the effective Hamiltonian depends on the convergence features of the iteration process. In the present work, we avoid a recursive formulation of the effective relativistic Hamiltonian and express the latter directly in terms of energy-independent linear operators. Such an expression is suitable for a one-step calculation of the effective Hamiltonian in actual quantum-chemical calculations.

(ii) The effective relativistic Hamiltonian obtained is used for the construction of a perturbational expansion of the exact relativistic electronic energy. An ordinary perturbational expansion based just on the effective non-Hermitian Hamiltonian $\hat{L}$ as well as a double perturbational expansion, which employs the symmetrized effective Hamiltonian together with the normalization operator, $1 + \hat{X}^\dagger \hat{X}$, of the relativistic wave function are constructed. Both theories, IORAn and IORAn(2), lead in zeroth order to the IORA method. Thus, it is IORA rather than ZORA, which is the true zeroth-order approach of the regular perturbation theory of relativistic effects.

The higher-order corrections to the IORA energy within both perturbation expansions converge rapidly to the exact relativistic energy for electronic states. Already the third-order perturbational expansion IORA3 outperforms in accuracy the popular Douglas–Kroll–Hess method, even when the latter is taken up to fifth order. The third-order expression obtained from double perturbation theory, IORA3(2), offers even better accuracy. In calculations on hydrogen-like atomic ions, IORA3(2) leads to the same level of accuracy as direct perturbation theory correct through order c^{-20}.

(iii) At the moment, the perspective of using the truncated expansion for the effective relativistic Hamiltonian $\hat{L}$ (and the wave function normalization operator $1 + \hat{X}^\dagger \hat{X}$) warrants further study. However, these expressions can be used for nonvariational calculations of the relativistic energy from the Rayleigh quotient. The use of the IORA wave function in the Rayleigh quotient (47) leads to the scaled IORA (SIORA) method. SIORA, although conceptually similar to the scaled ZORA approach, differs from the latter in two ways: (a) The IORA wave function provides a much better approximation to the exact relativistic wave function. (b) The Rayleigh quotient (47) used in SIORA leads to the exact relativistic equation (41); however, the Rayleigh quotient used in the scaled ZORA method leads to the IORA equation (20). In calculations on hydrogen-like atomic ions, the SIORA3/2 method reaches the same level of accuracy as direct perturbation theory correct through order c^{-22}.

(iv) The matrix form of the new methods was presented, because this can be easily incorporated into the existing quantum-chemical programs designed for nonrelativistic calculations. The atomic and molecular calculations performed

in the present work with the SIORA3/2 method as implemented in the COLOGNE 2003 suite of quantum-chemical programs, demonstrate that the new approach provides a considerable improvement over the results from both IORA and scaled ZORA calculations. The combination of an improved energy estimate with an accurate quasirelativistic wave function is crucial for obtaining reliable descriptions of atomic and molecular properties, especially those which depend on the core electrons. Indeed, properties such as the nuclear magnetic shielding tensor, dipole and quadrupole screening factors, the electric polarizability, etc., can be obtained by differentiation of the energy with respect to external pertur-

bations. The improved energy functional will then account for a better description of the energy spectrum, whereas the improved wave function will lead to a better description of the coupling to the external fields.

ACKNOWLEDGMENTS

APPENDIX A: COMPLETE ALGEBRAIC EXPRESSION FOR THE EFFECTIVE RELATIVISTIC HAMILTONIAN

The operator $\hat{L}^{(5)}$, obtained after five consecutive iterations according to Eq. (13), reads

$$
\begin{aligned}
\hat{L}^{(5)} =& (1-\hat{x}+\hat{x}^2-\hat{x}^3+\hat{x}^4-\hat{x}^5)\hat{L}^{(0)} + \hat{x}_2(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3+\hat{x}^4)\hat{L}^{(0)} - \hat{x}\hat{x}_2(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2 \\
& -\hat{x}^3)\hat{L}^{(0)} + \hat{x}^2\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)} - \hat{x}^3\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} - \hat{x}_3(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}(1-\hat{x} \\
& +\hat{x}^2-\hat{x}^3+\hat{x}^4)\hat{L}^{(0)} + \hat{x}\hat{x}_3(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)} - \hat{x}^2\hat{x}_3\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)} \\
& +\hat{x}_2\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3+\hat{x}^4)\hat{L}^{(0)} - \hat{x}\hat{x}_2\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)} - \hat{x}_2\hat{x}\hat{x}_2\hat{L}^{(0)} \\
& \times(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3+\hat{x}^4)\hat{L}^{(0)} + \hat{x}_2(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}\hat{x}_2(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)} - \hat{x}\hat{x}_2(1-\hat{x} \\
& +\hat{x}^2)\hat{L}^{(0)}\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)} - \hat{x}_2(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}\hat{x}\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)} + \hat{x}\hat{x}_2(1-\hat{x} \\
& +\hat{x}^2)\hat{L}^{(0)}\hat{x}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} + \hat{x}^2\hat{x}_2(1-\hat{x})\hat{L}^{(0)}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} + \hat{x}_2(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}\hat{x}^2\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} + \hat{x}_4(1 \\
& -\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3+\hat{x}^4)\hat{L}^{(0)} - \hat{x}\hat{x}_4\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x} \\
& +\hat{x}^2-\hat{x}^3)\hat{L}^{(0)} + \hat{x}_2(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}\hat{x}_2(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)} - \hat{x}\hat{x}_2(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}\hat{x}_2(1 \\
& -\hat{x})\hat{L}^{(0)}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} - \hat{x}_2(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}\hat{x}\hat{x}_2(1-\hat{x})\hat{L}^{(0)}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} - \hat{x}_2(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}\hat{x}_2(1-\hat{x} \\
& +\hat{x}^2)\hat{L}^{(0)}\hat{x}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} + \hat{x}_2(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}\hat{x}_2\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)} + \hat{x}_2\hat{x}_2(1 \\
& -\hat{x})\hat{L}^{(0)}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3+\hat{x}^4)\hat{L}^{(0)} + \hat{x}_2\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}\hat{x}_2(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2 \\
& -\hat{x}^3)\hat{L}^{(0)} - \hat{x}\hat{x}_2\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)} - \hat{x}_2\hat{x}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}\hat{x}_2(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2 \\
& -\hat{x}^3)\hat{L}^{(0)} - \hat{x}_2\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}\hat{x}\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)} + \hat{x}\hat{x}_2\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}\hat{x}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} \\
& +\hat{x}_2\hat{x}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}\hat{x}\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)} + \hat{x}_2\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}\hat{x}^2\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} \\
& -\hat{x}_2\hat{x}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}\hat{x}^2\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} - \hat{x}_2\hat{x}_3\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3+\hat{x}^4)\hat{L}^{(0)} \\
& -\hat{x}_3\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3+\hat{x}^4)\hat{L}^{(0)} - \hat{x}_2(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}\hat{x}_3(1-\hat{x})\hat{L}^{(0)}(1-\hat{x} \\
& +\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)} + \hat{x}\hat{x}_2(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}\hat{x}_3\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)} + \hat{x}_2(1-\hat{x}+\hat{x}^2 \\
& -\hat{x}^3)\hat{L}^{(0)}\hat{x}\hat{x}_3\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)} - \hat{x}_3(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3 \\
& +\hat{x}^4)\hat{L}^{(0)} + \hat{x}\hat{x}_3(1-\hat{x})\hat{L}^{(0)}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)} + \hat{x}_3(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}\hat{x}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2 \\
& -\hat{x}^3+\hat{x}^4)\hat{L}^{(0)} - \hat{x}_3(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}\hat{x}_2(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)} + \hat{x}\hat{x}_3(1-\hat{x})\hat{L}^{(0)}(1-\hat{x} \\
& +\hat{x}^2)\hat{L}^{(0)}\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)} + \hat{x}_3(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}\hat{x}\hat{x}_2(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)} \\
& -\hat{x}\hat{x}_3(1-\hat{x})\hat{L}^{(0)}(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}\hat{x}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} - \hat{x}^2\hat{x}_3\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)}\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} - \hat{x}_3(1-\hat{x}+\hat{x}^2)\hat{L}^{(0)}(1 \\
& -\hat{x}+\hat{x}^2-\hat{x}^3)\hat{L}^{(0)}\hat{x}^2\hat{x}_2\hat{L}^{(0)}(1-\hat{x})\hat{L}^{(0)} + \cdots,
\end{aligned}
\tag{A1}
$$

where all terms up to the fourth order in $\hat{L}^{(0)}$ are shown. One can anticipate that after the fifth iteration no new terms up to this order will appear in the expression. The operators $\hat{x}$ and $\hat{x}_k$, used in Eq. (A1), are defined in Eqs. (14) and (15) in the text.

APPENDIX B: ORDINARY PERTURBATION THEORY OF THE EFFECTIVE RELATIVISTIC HAMILTONIAN

Although the Rayleigh–Schrödinger perturbation theory is well known,[26] we repeat here some important results from it as they refer to Eq. (19). Note, that the wave function normalization in Eq. (19) differs from the standard nonrelativistic wave function normalization. Let us start from

$$(\hat{L}^{(0)}+\hat{L}^{(1)})\psi_i = \epsilon_i \hat{N}\psi_i, \tag{B1}$$

where $\hat{L}^{(0)}$ is the unperturbed Hamiltonian, $\hat{L}^{(1)}$ is the perturbation operator, and the superscript L at the wave function symbol is dropped for brevity. Multiplying $\hat{L}^{(1)}$ by a perturbation parameter λ, expanding the wave functions ψ_i and energies ϵ_i in powers of the parameter λ, and equating terms with the same power of λ on both sides of the resulting equation, one obtains

$$(\hat{L}^{(0)}-\epsilon_i^{(0)}\hat{N})\psi_i^{(0)} = 0, \tag{B2}$$

$$(\hat{L}^{(0)}-\epsilon_i^{(0)}\hat{N})\psi_i^{(1)} = -\hat{L}^{(1)}\psi_i^{(0)}+\epsilon_i^{(1)}\hat{N}\psi_i^{(0)}, \tag{B3}$$

$$(\hat{L}^{(0)}-\epsilon_i^{(0)}\hat{N})\psi_i^{(2)} = -\hat{L}^{(1)}\psi_i^{(1)}+\epsilon_i^{(1)}\hat{N}\psi_i^{(1)}+\epsilon_i^{(2)}\hat{N}\psi_i^{(0)}. \tag{B4}$$

Parametrizing the first-order wave function $\psi_i^{(1)}$ in terms of the eigenfunctions of the unperturbed Eq. (B2),

$$\psi_i^{(1)} = \sum_{k\neq i} \psi_k^{(0)} a_{ki} \tag{B5}$$

substituting Eq. (B5) into (B3), multiplying from the left with $(\psi_k^{(0)})^*$, and integrating, one obtains for the coefficients a_{ki} in the expansion (B5) the following:

$$(\epsilon_k^{(0)}-\epsilon_i^{(0)})a_{ki} = -\langle\psi_k^{(0)}|\hat{L}^{(1)}|\psi_i^{(0)}\rangle, \tag{B6}$$

where the orthonormality of the zeroth-order wave functions

$$\langle\psi_j^{(0)}|\hat{N}|\psi_i^{(0)}\rangle = \delta_{ij} \tag{B7}$$

was used. Substituting Eq. (B6) into Eq. (B5) one obtains

$$\psi_i^{(1)} = -\sum_{k\neq i} \psi_k^{(0)}\frac{\langle\psi_k^{(0)}|\hat{L}^{(1)}|\psi_i^{(0)}\rangle}{\epsilon_k^{(0)}-\epsilon_i^{(0)}}, \tag{B8}$$

which after substitution into Eq. (B4), multiplication of the resulting equation by $(\psi_i^{(0)})^*$ from the left, and integration, yields Eq. (22). Equation (21) for the first-order correction $\epsilon_i^{(1)}$ to the unperturbed energy $\epsilon_i^{(0)}$ is obtained from Eq. (B3) by multiplying it from the left with $(\psi_i^{(0)})^*$, integrating, and using the Hermitian property of the operators $\hat{L}^{(0)}$ and $\hat{N}$.

APPENDIX C: DOUBLE PERTURBATION THEORY OF THE EFFECTIVE RELATIVISTIC HAMILTONIAN

Let us rewrite Eq. (41) in the text in form of Eq. (C1),

$$\tfrac{1}{2}[(\hat{N}+\hat{N}^{(1)})\hat{N}^{-1}(\hat{L}^{(0)}+\hat{L}^{(1)})$$
$$+(\hat{L}^{(0)}+\hat{L}^{(1)})^{\dagger}\hat{N}^{-1}(\hat{N}+\hat{N}^{(1)})]\psi_i = \epsilon_i(\hat{N}+\hat{N}^{(1)})\psi_i, \tag{C1}$$

where the operator $\hat{N}^{(1)}$ represents the difference between the IORA normalization operator $\hat{N}$ and the exact relativistic normalization operator $1+\hat{X}^{\dagger}\hat{X}$ and the operator $\hat{L}^{(1)}$ is identical to the operator $\hat{Z}\hat{N}^{-1}\hat{L}^{(0)}$. Expanding wave functions ψ_i and energies ϵ_i in double perturbation series, one obtains from Eq. (C1)

$$(\hat{L}^{(0)}-\epsilon_i^{(00)}\hat{N})\psi_i^{(00)} = 0, \tag{C2}$$

$$(\hat{L}^{(0)}-\epsilon_i^{(00)}\hat{N})\psi_i^{(10)} = -\tfrac{1}{2}[\hat{N}^{(1)}\hat{N}^{-1}\hat{L}^{(0)}+\hat{L}^{(0)}\hat{N}^{-1}\hat{N}^{(1)}]\psi_i^{(00)}$$
$$+\epsilon_i^{(10)}\hat{N}\psi_i^{(00)}+\epsilon_i^{(00)}\hat{N}^{(1)}\psi_i^{(00)}, \tag{C3}$$

$$(\hat{L}^{(0)}-\epsilon_i^{(00)}\hat{N})\psi_i^{(01)} = -\tfrac{1}{2}[\hat{L}^{(1)}+(\hat{L}^{(1)})^{\dagger}]\psi_i^{(00)}+\epsilon_i^{(01)}\hat{N}\psi_i^{(00)}, \tag{C4}$$

$$(\hat{L}^{(0)}-\epsilon_i^{(00)}\hat{N})\psi_i^{(11)} = -\tfrac{1}{2}[\hat{N}^{(1)}\hat{N}^{-1}\hat{L}^{(1)}+(\hat{L}^{(1)})^{\dagger}\hat{N}^{-1}\hat{N}^{(1)}]\psi_i^{(00)}-\tfrac{1}{2}[\hat{N}^{(1)}\hat{N}^{-1}\hat{L}^{(0)}+\hat{L}^{(0)}\hat{N}^{-1}\hat{N}^{(1)}]\psi_i^{(01)}$$
$$-\tfrac{1}{2}[\hat{L}^{(1)}+(\hat{L}^{(1)})^{\dagger}]\psi_i^{(10)}+\epsilon_i^{(11)}\hat{N}\psi_i^{(00)}+\epsilon_i^{(10)}\hat{N}\psi_i^{(01)}+\epsilon_i^{(01)}\hat{N}\psi_i^{(10)}+\epsilon_i^{(00)}\hat{N}^{(1)}\psi_i^{(01)}+\epsilon_i^{(01)}\hat{N}^{(1)}\psi_i^{(00)}, \tag{C5}$$

where the first superscript at the energy or wave function denotes the order in the perturbation $\hat{N}^{(1)}$ and the second superscript denotes the order in the perturbation $\hat{L}^{(1)}$. Note, that the operator $\hat{N}^{(1)}$ is Hermitian, whereas the operator $\hat{L}^{(1)}$ is not.

Multiplying Eqs. (C3)–(C5) with $(\psi_k^{(00)})^*$ from the left and integrating, one obtains Eqs. (C6)–(C8) for the consecu-

tive first-order corrections to the unperturbed (i.e., IORA) energy,

$$\epsilon_i^{(10)} = \tfrac{1}{2}\langle\psi_i^{(00)}|\hat{N}^{(1)}\hat{N}^{-1}\hat{L}^{(0)}+\hat{L}^{(0)}\hat{N}^{-1}\hat{N}^{(1)}|\psi_i^{(00)}\rangle$$
$$-\epsilon_i^{(00)}\langle\psi_i^{(00)}|\hat{N}^{(1)}|\psi_i^{(00)}\rangle, \tag{C6}$$

$$\epsilon_i^{(01)} = \tfrac{1}{2}\langle\psi_i^{(00)}|\hat{L}^{(1)}+(\hat{L}^{(1)})^{\dagger}|\psi_i^{(00)}\rangle, \tag{C7}$$

J. Chem. Phys., Vol. 119, No. 22, 8 December 2003

Relativistic Hamiltonian   11539

$$\epsilon_i^{(11)} = \tfrac{1}{2}\langle\psi_i^{(00)}|\hat{N}^{(1)}\hat{N}^{-1}\hat{L}^{(1)} + (\hat{L}^{(1)})^\dagger\hat{N}^{-1}\hat{N}^{(1)}|\psi_i^{(00)}\rangle + \tfrac{1}{2}\langle\psi_i^{(00)}|\hat{N}^{(1)}\hat{N}^{-1}\hat{L}^{(0)} + \hat{L}^{(0)}\hat{N}^{-1}\hat{N}^{(1)}|\psi_i^{(01)}\rangle - \epsilon_i^{(10)}\langle\psi_i^{(00)}|\hat{N}|\psi_i^{(01)}\rangle$$

$$- \epsilon_i^{(00)}\langle\psi_i^{(00)}|\hat{N}^{(1)}|\psi_i^{(01)}\rangle + \tfrac{1}{2}\langle\psi_i^{(00)}|\hat{L}^{(1)} + (\hat{L}^{(1)})^\dagger|\psi_i^{(10)}\rangle - \epsilon_i^{(01)}\langle\psi_i^{(00)}|\hat{N}|\psi_i^{(10)}\rangle - \epsilon_i^{(01)}\langle\psi_i^{(00)}|\hat{N}^{(1)}|\psi_i^{(00)}\rangle. \tag{C8}$$

Equation (C8) can be further simplified with the help of Eqs. (C9) and (C10) obtained from Eqs. (C3) and (C4),

$$\langle\psi_i^{(10)}|\hat{L}^{(0)} - \epsilon_i^{(00)}\hat{N}|\psi_i^{(01)}\rangle = \epsilon_i^{(00)}\langle\psi_i^{(00)}|\hat{N}^{(1)}|\psi_i^{(01)}\rangle + \epsilon_i^{(10)}\langle\psi_i^{(00)}|\hat{N}|\psi_i^{(01)}\rangle - \tfrac{1}{2}\langle\psi_i^{(00)}|\hat{N}^{(1)}\hat{N}^{-1}\hat{L}^{(0)} + \hat{L}^{(0)}\hat{N}^{-1}\hat{N}^{(1)}|\psi_i^{(01)}\rangle, \tag{C9}$$

$$\langle\psi_i^{(01)}|\hat{L}^{(0)} - \epsilon_i^{(00)}\hat{N}|\psi_i^{(10)}\rangle = \epsilon_i^{(01)}\langle\psi_i^{(00)}|\hat{N}|\psi_i^{(10)}\rangle - \tfrac{1}{2}\langle\psi_i^{(00)}|\hat{L}^{(1)} + (\hat{L}^{(1)})^\dagger|\psi_i^{(10)}\rangle. \tag{C10}$$

Summing over all first-order corrections to the unperturbed energy, one obtains

$$\epsilon_i^{(00)} + \epsilon_i^{(10)} + \epsilon_i^{(01)} + \epsilon_i^{(11)} = \tfrac{1}{2}\langle\psi_i^{(00)}|(\hat{N} + \hat{N}^{(1)})\hat{N}^{-1}(\hat{L}^{(0)} + \hat{L}^{(1)}) + (\hat{L}^{(0)} + \hat{L}^{(1)})^\dagger\hat{N}^{-1}(\hat{N} + \hat{N}^{(1)})|\psi_i^{(00)}\rangle - \epsilon_i^{(00)}\langle\psi_i^{(00)}|\hat{N}^{(1)}|\psi_i^{(00)}\rangle$$

$$- \epsilon_i^{(01)}\langle\psi_i^{(00)}|\hat{N}^{(1)}|\psi_i^{(00)}\rangle - \langle\psi_i^{(10)}|\hat{L}^{(0)} - \epsilon_i^{(00)}\hat{N}|\psi_i^{(01)}\rangle - \langle\psi_i^{(01)}|\hat{L}^{(0)} - \epsilon_i^{(00)}\hat{N}|\psi_i^{(10)}\rangle. \tag{C11}$$

The last two terms in Eq. (C11) are identical, because $\hat{L}^{(0)}$ and $\hat{N}$ are Hermitian operators. For the purpose of estimating these terms, let us represent the first-order perturbed wave functions as in the following:

$$\psi_i^{(10)} = \sum_{k \neq i} \psi_k^{(00)} a_{ki}, \tag{C12a}$$

$$\psi_i^{(01)} = \sum_{k \neq i} \psi_k^{(00)} b_{ki}. \tag{C12b}$$

The expansion coefficients a_{ki} and b_{ki} can be found using Eqs. (C3) and (C4), respectively. Thus, one has for $\psi_i^{(10)}$ and $\psi_i^{(01)}$

$$\psi_i^{(10)} = \tfrac{1}{2}\sum_{k \neq i} \psi_k^{(00)}\langle\psi_k^{(00)}|\hat{N}^{(1)}\hat{N}^{-1}\hat{L}^{(0)} + \hat{L}^{(0)}\hat{N}^{-1}\hat{N}^{(1)}$$

$$- 2\epsilon_i^{(00)}\hat{N}^{(1)}|\psi_i^{(00)}\rangle/(\epsilon_i^{(00)} - \epsilon_k^{(00)}), \tag{C13a}$$

$$\psi_i^{(01)} = \tfrac{1}{2}\sum_{k \neq i} \psi_k^{(00)}\langle\psi_k^{(00)}|\hat{L}^{(1)}$$

$$+ (\hat{L}^{(1)})^\dagger|\psi_i^{(00)}\rangle/(\epsilon_i^{(00)} - \epsilon_k^{(00)}), \tag{C13b}$$

which upon substitution into Eq. (C11) yield for the last two terms

$$-\langle\psi_i^{(10)}|\hat{L}^{(0)} - \epsilon_i^{(00)}\hat{N}|\psi_i^{(01)}\rangle - \langle\psi_i^{(01)}|\hat{L}^{(0)} - \epsilon_i^{(00)}\hat{N}|\psi_i^{(10)}\rangle$$

$$= \tfrac{1}{2}\sum_{k \neq i} \langle\psi_i^{(00)}|\hat{N}^{(1)}\hat{N}^{-1}\hat{L}^{(0)} + \hat{L}^{(0)}\hat{N}^{-1}\hat{N}^{(1)}$$

$$- 2\epsilon_i^{(00)}\hat{N}^{(1)}|\psi_k^{(00)}\rangle\langle\psi_k^{(00)}|\hat{L}^{(1)}$$

$$+ (\hat{L}^{(1)})^\dagger|\psi_i^{(00)}\rangle/(\epsilon_i^{(00)} - \epsilon_k^{(00)}). \tag{C14}$$

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