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Perturbation energy expansions based on two-component relativistic Hamiltonians

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Abstract. The approximate elimination of the small-component approach provides ansätze for the relativistic wave function. The assumed form of the small component of the wave function in combination with the Dirac equation define transformed but exact Dirac equations. The present derivation yields a family of two-component relativistic Hamiltonians which can be used as zeroth-order approximation to the Dirac equation. The operator difference between the Dirac and the two-component relativistic Hamiltonians can be used as a perturbation operator. The first-order perturbation energy corrections have been obtained from a direct perturbation theory scheme based on these two-component relativistic Hamiltonians. At the two-component relativistic level, the errors of the relativistic correction to the energies are proportional to $\alpha^4 Z^4$, whereas for the relativistic energy corrections including the first-order perturbation theory contributions, the errors are of the order of $\alpha^6 Z^6$–$\alpha^8 Z^8$ depending on the zeroth-order Hamiltonian.

Keywords: Dirac equation – Elimination of the small component – Relativistic corrections – Transformed Dirac equations – Exponential regular approximation

1 Introduction

The Dirac equation with four spinor components demands large computational efforts to solve. Relativistic effects in electronic structure calculations are therefore often considered by means of approximate two-component equations. The approximate relativistic (also called quasi-relativistic) Hamiltonians consist of the nonrelativistic Hamiltonian augmented with additional operators describing the dominant relativistic effects. Two-component relativistic calculations provide a firm basis for the calculations of higher-order relativistic corrections by means of perturbation theory (PT). Several two-component relativistic approximations have been proposed. The most successful approaches are the Douglas–Kroll–Hess method [1, 2, 3, 4, 5, 6], the relativistic direct PT [7, 8, 9, 10, 11, 12], the zeroth-order regular approximation (ZORA) [13, 14, 15, 16, 17, 18, 19, 20, 21, 22], and the normalized elimination of small components methods [23, 24, 25, 26]. Related quasi-relativistic schemes based on the elimination of the small components and other similar nonsingular two-component relativistic Hamiltonians have also been proposed [27, 28, 29, 30, 31, 32, 33].

In this work, it is shown how a family of two-component relativistic Hamiltonians can conveniently be derived. The operator difference between the two-component relativistic Hamiltonians and the Dirac equation can be explicitly identified and used in perturbation expansions. Expressions are derived for a direct PT scheme based on two-component relativistic Hamiltonians. The remaining difference between the variational energy obtained using two-component relativistic Hamiltonians and the energy of the Dirac equation is estimated numerically by applying the direct PT approach. A general transformed Dirac equation is derived in Sects. 2 and 3. Two-component relativistic Hamiltonians such as the exponential regular approximation (ERA) and ZORA and other related two-component relativistic Hamiltonians are presented in Sect. 4 and some of their advantages and disadvantages are briefly discussed. Expressions are derived for the direct PT based on two-component relativistic Hamiltonians in Sect. 5. The computational methods are described in Sect. 6 and the results of the calculations on one-electron atoms are discussed in Sect. 7.

2 The general ansatz

Transformed Dirac equations can be obtained by using approximate solutions for the small components as ansätze for the wave function. The ansatz can be deduced from the lower half of the Dirac equation by an approximate elimination of the small component.

Contribution to the Björn Roos Honorary Issue

The four-component Dirac equation can be written in atomic units as

$$\begin{pmatrix} V(r) & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & V(r)-2c^2 \end{pmatrix}\begin{pmatrix}\psi_{\mathrm{L}}\\ \psi_{\mathrm{S}}\end{pmatrix} = E\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}\psi_{\mathrm{L}}\\ \psi_{\mathrm{S}}\end{pmatrix} \ , \tag{1}$$

where ψ_{L} and ψ_{S} are the large and small components, respectively. $V(r)$ is an external potential, c is the speed of light ($c = 137.0359895$ au), $\vec{p}$ is the momentum operator, and $\vec{\sigma}$ is a vector of the three Pauli spin matrices. The elimination of the small component yields an energy-dependent expression (Eq. 2) which relates the large and the small components:

$$\psi_{\mathrm{S}} = \frac{c}{2c^2 - V(r) + E}\vec{\sigma}\cdot\vec{p}\psi_{\mathrm{L}} \tag{2}$$

Equation (2) or approximations to this expression can be used as an ansatz for the small component. By inserting it into the Dirac equation, modified but still exact Dirac equations are obtained. Analogously, the nonrelativistic Schrödinger equation can be obtained by applying the elimination of the small component transformation on the Lévy–Leblond equation [34, 35]. The four-component Lévy–Leblond equation,

$$\begin{pmatrix} V(r) & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & -2c^2 \end{pmatrix}\begin{pmatrix}\psi_{\mathrm{L}}\\ \psi_{\mathrm{S}}\end{pmatrix} = E\begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix}\begin{pmatrix}\psi_{\mathrm{L}}\\ \psi_{\mathrm{S}}\end{pmatrix} \ , \tag{3}$$

is a Galilei-invariant equivalent of the Schrödinger equation for a electron with spin [9, 36, 37] and has, in principle, the same energy spectrum as the Schrödinger equation, but it is, as the Dirac equation, not bounded from below [9]. In Eq. (3), we use the same scaling convention as used for the Dirac equation. One can see in Eq. (3) that the large and the small components are related through the kinetic-energy balance condition (KEBC)

$$\psi_{\mathrm{S}} = \frac{1}{2c}\vec{\sigma}\cdot\vec{p}\psi_{\mathrm{L}} \ . \tag{4}$$

The KEBC can also be used as an ansatz for the small components of the Dirac equation, but the substitution of Eq. (4) into Eq. (1) results in numerical difficulties at the nuclei [10, 14, 15]. However, in a finite basis set the numerical difficulties due to the singularities at the nuclei can be circumvented [12]. Another method to avoid the singularities at the nuclei was proposed by van Lenthe and coworkers [14, 15, 17], who suggested a method that also includes the interaction potential, $V(r)$, in the denominator of the ansatz for the small component. This ansatz (Eq. 5) was used in the derivation of the so-called ZORA Hamiltonian.

$$\psi_{\mathrm{S}} = \frac{c}{2c^2 - V(r)}\vec{\sigma}\cdot\vec{p}\psi_{\mathrm{L}} \ . \tag{5}$$

For atoms and molecules, the total potential, $V(r)$, close to the nucleus is completely dominated by the nuclear–electron attraction potential, even for many-electron systems. At the nucleus, the potential is thus proportional to $-\frac{Z}{r}$. This implies that when the ZORA ansatz is employed, the small components approach zero at the nuclei. The singular behaviour encountered in quasi-relativistic approaches based on the KEBC is therefore avoided.

A general ansatz for the small component can be defined as

$$\psi_{\mathrm{S}} = \frac{f(r)}{2c}\vec{\sigma}\cdot\vec{p}\psi_{\mathrm{L}} \ , \tag{6}$$

where $f(r)$ has the property of approaching a constant value of unity at very large distances from the nuclei, whereas at small distances it becomes zero. For the KEBC ansatz, $f(r)$ is independent of r. In the ZORA approach, $f(r)$ approaches unity at large distances when $2c^2 \gg \frac{Z}{r}$ and becomes zero at the nuclei.

In this work, the ZORA and the KEBC ansätze, which are already approximations to the energy-dependent elimination of the small-component approach, are replaced by another but similar expression that relates the large and the small components. The general ansatz function should have the same shape as the ZORA function close to the nucleus. A general function $f(r)$ that fulfils the desired asymptotic conditions for $r \to 0$ and for $r \to \infty$ is

$$f(r) = 1 - \exp^{[-(\frac{2c^2 r}{\gamma Z})]} \ , \tag{7}$$

where c is the speed of light, Z is the nuclear charge, and γ is an arbitrary constant which can be adjusted. This ERA ansatz and its first derivative with respect to r are close to the nucleus reminiscent of those of the ZORA function. $\gamma = 1$ yields the same first derivative at the nucleus as obtained with the ZORA function. The KEBC, ZORA (IORA) and ERA ansatz functions are compared in Fig. 1.

3 The transformed Dirac equation

By using Eq. (6) as an ansatz for the small components and inserting it into the energy expression for the Dirac

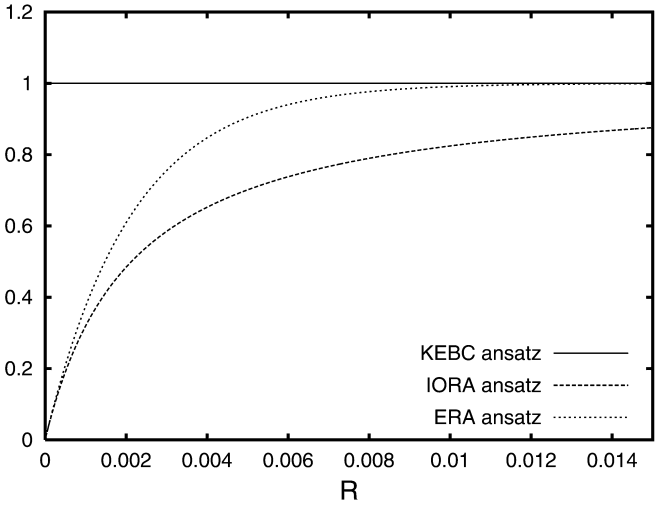

Fig. 1. The exponential regular approximation (*ERA* with $\gamma = 1$), the zeroth-order-regular approximation (*ZORA*), and the kinetic-energy balance condition (*KEBC*) ansatz functions for mercury ($Z = 80$). The distance R is given in bohrs

equation (Eq. 1) one obtains an effective transformed four-component Hamiltonian ($\hat{H}_{\mathrm{Dirac}}$).

$$\hat{H}_{\mathrm{Dirac}} = \begin{pmatrix} V(r) & \frac{1}{2}(\vec{\sigma}\cdot\vec{p})^{\dagger} f(r)(\vec{\sigma}\cdot\vec{p}) \\ \frac{1}{2}(\vec{\sigma}\cdot\vec{p})^{\dagger} f(r)(\vec{\sigma}\cdot\vec{p}) & \frac{1}{4c^2}(\vec{\sigma}\cdot\vec{p})^{\dagger}\left[V(r)-2c^2\right] f^2(r)(\vec{\sigma}\cdot\vec{p}) \end{pmatrix} \tag{8}$$

with a general metric ($\hat{S}$)

$$\hat{S} = \begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{4c^2}(\vec{\sigma}\cdot\vec{p})^{\dagger} f^2(r)(\vec{\sigma}\cdot\vec{p}) \end{pmatrix} . \tag{9}$$

To simplify the expression for the effective Hamiltonian (Eqs. 8, 9), one can separate out a constant of 1 from $f(r)$; $f(r) - 1$ describes the ansatz difference between the KEBC and the general ansatz. By using the identity

$$-\nabla^2 = (\vec{\sigma}\cdot\vec{p})^{\dagger}(\vec{\sigma}\cdot\vec{p}) \tag{10}$$

and denoting

$$\hat{T} = -\frac{1}{2}\nabla^2 , \tag{11}$$

$$\hat{A} = \frac{1}{2}(\vec{\sigma}\cdot\vec{p})^{\dagger}[f(r)-1](\vec{\sigma}\cdot\vec{p}) , \tag{12}$$

$$\hat{B} = \frac{1}{2}(\vec{\sigma}\cdot\vec{p})^{\dagger}\left[1-f^2(r)\right](\vec{\sigma}\cdot\vec{p}) , \tag{13}$$

$$\hat{X} = \frac{1}{4c^2}(\vec{\sigma}\cdot\vec{p})^{\dagger}\left[f^2(r)V(r)\right](\vec{\sigma}\cdot\vec{p}) , \tag{14}$$

$$\hat{Y} = \frac{1}{4c^2}(\vec{\sigma}\cdot\vec{p})^{\dagger} f^2(r)(\vec{\sigma}\cdot\vec{p}) = \frac{1}{2c^2}(\hat{T}-\hat{B}) , \tag{15}$$

and

$$\hat{V} = V(r) \tag{16}$$

the modified but still exact Dirac equation can be written as

$$\begin{pmatrix} \hat{V} & \hat{T}+\hat{A} \\ \hat{T}+\hat{A} & -\hat{T}+\hat{B}+\hat{X} \end{pmatrix} \begin{pmatrix} \phi_L \\ \phi_S \end{pmatrix} = E \begin{pmatrix} \hat{1} & 0 \\ 0 & \hat{Y} \end{pmatrix} \begin{pmatrix} \phi_{\mathrm{L}} \\ \phi_{\mathrm{S}} \end{pmatrix} . \tag{17}$$

4 Two-component relativistic Hamiltonians

The first approximation one can make in order to derive two-component relativistic equations is to assume that the upper (ϕ_{L}) and the lower (ϕ_{S}) components in Eq. (17) are identical. Denoting them by ϕ_{QR}, the general two-component relativistic Hamiltonian becomes

$$\begin{aligned} \hat{H}_{\mathrm{QR}}\phi_{\mathrm{QR}} &= (\hat{H}_{\mathrm{NR}} + 2\hat{A} + \hat{B} + \hat{X})\phi_{\mathrm{QR}} \\ &= E_{\mathrm{QR}}(\hat{1} + \hat{Y})\phi_{\mathrm{QR}} , \end{aligned} \tag{18}$$

where $\hat{H}_{\mathrm{NR}} = \hat{T} + \hat{V}$ is the nonrelativistic Hamiltonian. The scalar-relativistic and spin–orbit contributions can be separated by applying the Dirac relation

$$(\vec{\sigma}\cdot\vec{A})^{\dagger}(\vec{\sigma}\cdot\vec{B}) = \vec{A}\cdot\vec{B} + i\vec{\sigma}\cdot(\vec{A}\times\vec{B}) . \tag{19}$$

By omitting the spin–orbit term, one-component relativistic models are obtained [23], but they will not be considered in this work. Expressions for the calculation of first-order properties at the quasi-relativistic level of theory are presented elsewhere [38].

4.1 Exponential regular approximation

The ERA Hamiltonian can be obtained from Eq. (17) by inserting the exponential function defined in Eq. (7) into the general ansatz for the small component (Eq. 6). One important advantage with the ERA is that the exponential function declines much faster with r than the ZORA ansatz. Therefore, the ERA ansatz does not cause the same kind of complications as one experiences when evaluating the gradients needed in molecular structure optimizations using the ZORA Hamiltonian [17]; for typical bond distances the ERA function is equal to 1. In addition, the ansatz does not contain nuclear attraction potentials or other terms that introduce gauge dependencies.

4.2 Modified ERA

The two-component relativistic Hamiltonians obtained using the general ansatz usually have a metric that include spin–orbit contributions. This can be a undesirable situation since in a PT study of spin–orbit effects, the addition of the spin–orbit coupling requires reorthogonalization of the orbitals [39]. However, as seen in Eq. (15), the relativistic correction term ($\hat{Y}$) consists of two contributions, $\hat{T}$ and $\hat{B}$. $\hat{B}$ is several orders of magnitude less significant than $\hat{T}$. Furthermore, the $\hat{B}$ operator can also be separated into scalar-relativistic and spin–orbit contributions and only the small spin–orbit term of the $\hat{B}$ operator need be neglected; new two-component relativistic models, the metric of which does not contain any spin–orbit terms, can be obtained either by completely omitting the $\hat{B}$ operator in the metric or by neglecting only the spin–orbit contribution to the $\hat{B}$ operator. In the present metric modified ERA (MERA) method, the $\hat{B}$ operator is completely neglected in the metric.

4.3 Zeroth-order regular approximation

The ZORA Hamiltonian can be derived from the upper part of the transformed Dirac equation (Eq. 17). By using the ZORA ansatz for the small component (Eq. 5) and assuming that the upper and the lower components are equal, the final ZORA equation for the upper component becomes

$$\hat{H}_{\mathrm{ZORA}}\phi_{\mathrm{ZORA}} = (\hat{H}_{\mathrm{NR}} + \hat{A})\phi_{\mathrm{ZORA}} = E_{\mathrm{ZORA}}\phi_{\mathrm{ZORA}} . \tag{20}$$

The assumption that the upper and the lower components were equal can actually be used to define a formal lower half of the ZORA equation. The lower ZORA equation

$$\hat{A}\phi_{\mathrm{ZORA}} - \hat{A}\phi_{\mathrm{ZORA,lower}} = 0 \tag{21}$$

is never used but Eq. (21) is the simplest equation that makes the formal four-component ZORA operator Hermitian and at the same time it defines that the upper (ϕ_{ZORA}) and the lower ($\phi_{\mathrm{ZORA,lower}}$) components are identical. This derivation of the ZORA equation shows that Eq. (20) is not a completely variational consequence of the Dirac equation.

4.4 Infinite-order regular approximation

When one instead proceeds as for the general case and inserts the ZORA ansatz into the Rayleigh quotient, one sees that two new operator terms, $\hat{B}$ and $\hat{X}$, appear in the Hamiltonian and in addition one new term ($\hat{Y}$) appears in the metric. For the ZORA ansatz, the sum of the $\hat{A}$, $\hat{B}$ and $\hat{X}$ operators vanishes:

$$\hat{A} + \hat{B} + \hat{X} = \hat{0} \ . \tag{22}$$

Thus, compared to the ZORA method the only new contribution in the fully variational approach is the ($\hat{Y}$) correction to the metric. The two-component relativistic model obtained by using the ZORA ansatz in combination with a fully variational derivation is the infinite-order regular approximation (IORA) previously derived by Sadlej and Snijders [20] and by Dyall and Lenthe [21]. The IORA method has recently been implemented by Klopper et al. [22]. The ZORA model can be obtained from the IORA equation by omitting the relativistic correction term to the metric. However, the indirect renormalization contribution is as significant as the relativistic interaction operator in the Hamiltonian. This is the reason why ZORA overestimates the relativistic correction of the 1*s* energy of U by more than a factor of 2 [16]. For valence orbitals the ZORA model works much better.

4.5 Modified IORA

As for the ERA model, a metric modified IORA (MIORA) model whose metric is independent of the spin–orbit coupling can be obtained by neglecting the $\hat{B}$ term in the metric i.e. by replacing the $\hat{Y}$ operator by $\frac{1}{2c^2}\hat{T}$. Alternatively, another model which does not contain any spin–orbit terms in the metric can be obtained by neglecting only the spin–orbit coupling term of the $\hat{B}$ operator.

5 Perturbation energy expansions

In order to derive a useful perturbation theory expression with Eq. (18) as the zeroth-order equation, the modified Dirac equation (Eq. 17) has to be reformulated in such a way that the operator difference between Eqs. (17) and (18) can be identified and used as a perturbation operator.

In the last step of the derivation of the two-component relativistic Hamiltonian (Eq. 18), it was assumed that the upper (ϕ_{L}) and the lower (ϕ_{S}) components are identical. This was the only approximation made in that derivation. Instead of making this assumption, the difference between the upper and the lower components can be denoted by Δ_{S}.

$$\phi_{\mathrm{S}} = \phi_{\mathrm{L}} + \Delta_{\mathrm{S}} \tag{23}$$

By inserting Eq. (23) into the modified Dirac equation (Eq. 17) a new exact expression for the Dirac equation (Eq. 24) is obtained:

$$\begin{pmatrix} \hat{H}_{\mathrm{QR}} & \hat{A}+\hat{B}+\hat{X} \\ \hat{A}+\hat{B}+\hat{X} & -\hat{T}+\hat{B}+\hat{X} \end{pmatrix} \begin{pmatrix} \phi_{\mathrm{L}} \\ \Delta_{\mathrm{S}} \end{pmatrix} = E \begin{pmatrix} \hat{1}+\hat{Y} & \hat{Y} \\ \hat{Y} & \hat{Y} \end{pmatrix} \begin{pmatrix} \phi_{\mathrm{L}} \\ \Delta_{\mathrm{S}} \end{pmatrix} \ . \tag{24}$$

The two-component relativistic Hamiltonian and the operators describing the difference between the exact Dirac Hamiltonian and the two-component relativistic one are now explicitly separated and the direct PT method can be applied. In the direct PT approach, the metric is also affected by the perturbation [9]. Note that the interaction matrix is block diagonal at the IORA level of theory, whereas the coupling between the upper and the lower components still appears in the metric.

The Hamiltonian and the metric of Eq. (24) can be separated into a zeroth-order part and a perturbation operator as

$$\hat{H}_0 = \begin{pmatrix} \hat{H}_{\mathrm{QR}} & 0 \\ 0 & 0 \end{pmatrix}; \quad \hat{H}_1 = \begin{pmatrix} 0 & \hat{A}+\hat{B}+\hat{X} \\ \hat{A}+\hat{B}+\hat{X} & -\hat{T}+\hat{B}+\hat{X} \end{pmatrix} \tag{25}$$

and

$$\hat{S}_0 = \begin{pmatrix} 1+\hat{Y} & 0 \\ 0 & 0 \end{pmatrix}; \quad \hat{S}_1 = \begin{pmatrix} 0 & \hat{Y} \\ \hat{Y} & \hat{Y} \end{pmatrix} \ . \tag{26}$$

In the spirit of the direct PT approach [7, 8, 9, 10, 11, 18], Eq. (24) can be expanded in an infinite perturbation series expansion

$$\sum_i (\hat{H}_0 + \hat{H}_1)\phi^{(i)} = \sum_{i,j} (\hat{S}_0 + \hat{S}_1)\phi^{(i)}E^{(j)} \ , \tag{27}$$

where $\phi^{(i)}$ denotes the order-by-order terms of the four-component function corresponding to the large upper component ϕ_{L} and to the small lower component Δ_{S}. $E^{(j)}$ are the perturbation energies of order j. In general, the order-by-order contributions would be determined by solving Eq. (27) for each order of the perturbation expansion; however, the present perturbation expansion contains additional complications. The $\hat{H}$ and $\hat{S}$ matrices are partitioned into four blocks; the large–large (LL), the large–small (LS), the small–large (SL), and the small–small (SS) matrix blocks describe the interaction of the large and small components. A similar block structure previously appeared in the PT study of the extended Koopmans' theorem [40]. In the zeroth-order matrices $\hat{H}_0$ and $\hat{S}_0$, only the LL block is nonzero, whereas the perturbation matrices $\hat{H}_1$ and $\hat{S}_1$ are nonzero in the three other matrix blocks. Only the large part of $\phi^{(0)}$, which is denoted $\phi_{\mathrm{L}}^{(0)}$, can be determined from the zeroth-order equation (Eq. 18). The small component

($\Delta_S^{(0)}$) must be determined from an expression deduced from the perturbation expansion. Owing to the block structure, separate connected equations can be derived for each order of the small ($\Delta_S^{(k)}$) and the large ($\phi_L^{(k)}$) components. The small component of the order $n-1$ ($\Delta_S^{(n-1)}$) can be obtained from the lower half of the nth-order PT equations as

$$\Delta_S^{(n-1)} = \left(\hat{H}_{SS} - E^{(0)}\hat{S}_{SS}\right)^{-1} \times \left(-\hat{H}_{SL}\phi_L^{(n-1)} + \sum_{k=0}^{n-1}\hat{S}_{SL}E^{(k)}\phi_L^{(n-k-1)} + \sum_{k=1}^{n-1}\hat{S}_{SS}E^{(k)}\Delta_S^{(n-k-1)}\right) . \quad (28)$$

As seen in Eq. (28), only contributions from the lower orders are needed. When $\Delta_S^{(n-1)}$ has been determined, the perturbation energy of order n ($E^{(n)}$) can be obtained by multiplying the nth-order PT equation from the left by $\phi^{(0)\dagger}$ as

$$E^{(n)} = \left(\phi^{(0)\dagger}\hat{H}_1\phi^{(n-1)} - \sum_{k=1}^{n-1}E^{(k)}\phi^{(0)\dagger}\hat{S}_0\phi^{(n-k)} - \sum_{k=0}^{n-1}E^{(k)}\phi^{(0)\dagger}\hat{S}_1\phi^{(n-k-1)}\right) \Big/ \left(\phi^{(0)\dagger}\hat{S}_0\phi^{(0)}\right) . \quad (29)$$

When also higher-order energy corrections are desired, the next ϕ_L term in the PT expansion can be obtained from the upper half of the PT expansion as

$$\phi_L^{(n)} = \left(\hat{H}_{LL} - E^{(0)}\hat{S}_{LL}\right)^{-1}\left(-\hat{H}_{LS}\Delta_S^{(n-1)} + \sum_{k=1}^{n}\hat{S}_{LL}E^{(k)}\phi_L^{(n-k)} + \sum_{k=0}^{n-1}\hat{S}_{LS}E^{(k)}\Delta_S^{(n-k-1)}\right) . \quad (30)$$

The small component of order n ($\Delta_S^{(n)}$) can then be determined from Eq. (28) and the algorithm cycle for the perturbation expansion is closed. The explicit equations for the first-order correction are

$$\Delta_S^{(0)} = \left(\hat{H}_{SS} - E^{(0)}\hat{S}_{SS}\right)^{-1}\left(-\hat{H}_{SL}\phi_L^{(0)} + \hat{S}_{SL}E^{(0)}\phi_L^{(0)}\right) \quad (31)$$

and

$$E^{(1)} = \left(\phi_L^{(0)\dagger}\hat{H}_{LS}\Delta_S^{(0)} + \Delta_S^{(0)\dagger}\hat{H}_{SL}\phi_L^{(0)} + \Delta_S^{(0)\dagger}\hat{H}_{SS}\Delta_S^{(0)} - E^{(0)}\phi_L^{(0)\dagger}\hat{S}_{LS}\Delta_S^{(0)} - E^{(0)}\Delta_S^{(0)\dagger}\hat{S}_{SL}\phi_L^{(0)} - E^{(0)}\Delta_S^{(0)\dagger}\hat{S}_{SS}\Delta_S^{(0)}\right) \Big/ \left(\phi_L^{(0)\dagger}\hat{S}_{LL}\phi_L^{(0)}\right) , \quad (32)$$

where

$$\hat{H}_{LS} = \hat{H}_{SL} = \hat{A} + \hat{B} + \hat{X}; \hat{H}_{SS} = -\hat{T} + \hat{B} + \hat{X} \quad (33)$$

$$\hat{S}_{LL} = \hat{1} + \hat{Y}; \hat{S}_{LS} = \hat{S}_{SL} = \hat{S}_{SS} = \hat{Y} \quad (34)$$

and the zeroth-order large component is normalized with $\hat{S}_{LL}$ as metric

$$\phi_L^{(0)\dagger}\hat{S}_{LL}\phi_L^{(0)} = 1 . \quad (35)$$

The first-order perturbation expressions can be simplified further; the $\hat{H}_{SS}$ block consists of three contributions of which $-\hat{T}$ is of the order α^0, whereas the $\hat{X}$, $\hat{B}$, and $\hat{A}$ operators are proportional to α^2, where $\alpha = c^{-1}$ is the fine-structure constant. An approximate first-order energy correction can therefore be obtained by neglecting the $\hat{B}$ and $\hat{X}$ terms in $\hat{H}_{SS}$. Here it is also appropriate to mention that Dyall and Lenthe [26] have recently derived and implemented an alternative perturbation expansion approach for the IORA equation. They analysed the perturbation-energy expansions for U^{91+} and for neutral uranium up to third order.

6 Computational methods

In order to test the accuracy of the equations derived in the previous sections we used the finite-element method to solve them for one-electron atoms. The radial range was divided into elements. The lengths of the elements were distributed exponentially. Each element is a factor of 1.3 longer than the previous one starting at the nucleus. In each element a linear grid is used. Lagrange interpolation polynomials of fourth order were used as local basis functions (element functions). This corresponds to local expansions of fourth-order polynomials. The nonrelativistic integrals were calculated analytically, whereas the relativistic correction integrals were obtained by numerical Gauss integration. The practical infinity was chosen to be at $R_\infty = \frac{100}{Z}$, where Z is the nuclear charge. The calculations were performed using a grid consisting of 80 elements containing five element functions each. The point nucleus model was adopted in all calculations.

7 Applications

7.1 Infinite-order regular approximation

The equations derived in Sects. 2, 3, 4, and 5 were implemented as described in Sect. 6 and the methods were applied on one-electron atoms. The energies for the lowest 1s states obtained using the IORA Hamiltonian [26] are given in Table 1. For the lightest elements (up to Ca^{19+}), the IORA and the Dirac energies differ by less than a few mhartrees, whereas for U^{91+} the IORA energy is about 59 hartrees (in absolute value) larger than the Dirac value. The difference between the IORA and Dirac energies increases with the sixth power in Z, indicating that the IORA model is correct up to $\alpha^2 Z^4$.

7.2 Exponential regular approximation

The energies obtained using the ERA Hamiltonian are given in Table 2. The ERA model has one parameter that can be freely adjusted, namely the scaling parameter γ in the denominator of the exponent in Eq. (7). The energies presented in Table 2 were obtained with the scaling factor $\gamma = 1$. The errors in the energies obtained with the ERA Hamiltonian are for the lighter systems about 5 times larger than the errors in the IORA

Table 1. The quasi-relativistic total energies (hartrees) for the lowest 1s state of one-electron atoms calculated at the infinite-order regular approximation (IORA) level and the corresponding first-order perturbation-energy correction, E(PT). The IORA and IORA + PT energies are compared to the corresponding Dirac values

Atom	E(IORA)	Difference[a]	E(PT)	Difference[b]
H	−0.500006657	0.0000000	0.0000000	0.0000000
Ne^{9+}	−50.0668306	0.0000886	0.0000886	-3.4×10^{-8}
Ca^{19+}	−201.0821962	0.0056728	0.0056734	−0.0000006
Zn^{29+}	−455.5895942	0.0646871	0.0471462	−0.0000275
Zr^{39+}	−818.1719645	0.3644667	0.3649423	−0.0004756
Sn^{49+}	−1296.0244180	1.3982621	1.4026258	−0.0043637
Nd^{59+}	−1899.9000166	4.2176607	4.2444008	−0.0267401
Yb^{69+}	−2645.6585812	10.8120163	10.9366048	−0.1245885
Hg^{79+}	−3556.9010448	24.7088941	25.1870033	−0.4781092
Th^{89+}	−4669.7676396	52.0099853	53.6059752	−1.5959899
U^{91+}	−4921.0993398	59.9013167	61.9063207	−2.0050040
Fm^{99+}	−6042.5852735	103.3898891	108.2216352	−4.8317462
118^{117+}	−9563.0237251	332.3964009	363.7824657	−31.3860647

[a] E(Dirac)-E(IORA)
[b] E(Dirac)-E(IORA + PT)

Table 2. The quasi-relativistic total energies (hartrees) for the lowest 1s state of one-electron atoms calculated at the exponental regular approximation (*ERA*) level and the corresponding first-order perturbation-energy correction, E(PT). The ERA and ERA + PT energies are compared to the corresponding Dirac values

Atom	E(ERA)	Difference[a]	E(PT)	Difference[b]
H	−0.500006657	0.0000000	0.0000000	0.0000000
Ne^{9+}	−50.0671935	0.0004515	0.0004531	−0.0000016
Ca^{19+}	−201.1057376	0.0292142	0.0295874	−0.0003732
Zn^{29+}	−455.8511025	0.3261954	0.3345066	−0.0083112
Zr^{39+}	−819.5330302	1.7255324	1.7934351	−0.0679027
Sn^{49+}	−1300.5431403	5.9169844	6.2224791	−0.3054946
Nd^{59+}	−1910.7706194	15.0882635	15.9806405	−0.8923770
Yb^{69+}	−2665.5618257	30.7152608	32.5328847	−1.8176239
Hg^{79+}	−3584.1418966	51.9497459	54.5862842	−2.6365383
Th^{89+}	−4692.3865829	74.6289286	77.2688131	−2.6398845
U^{91+}	−4939.9511031	78.7530800	81.2539373	−2.5008573
Fm^{99+}	−6030.9316491	91.7362647	93.2648117	−1.5285470
118^{117+}	−9315.6475896	85.0202654	84.2284885	+0.7917770

[a] E(Dirac)-E(IORA)
[b] E(Dirac)-E(IORA + PT)

energies. For the heavier atoms, the errors in the ERA energies are of the same size as obtained with the IORA model. For elements heavier than Fm^{99+} the ERA energies agree better with Dirac values than the IORA energies do.

The difference between the energies obtained at the ERA level and the Dirac energies (ΔE) are plotted in Fig. 2 as a function of the nuclear charge. The same graph for the other models is also shown in the figure. It can clearly be seen that for smaller Z values both the ERA and the IORA models scale with the same power of αZ, whereas for the heavier elements the slope of the ERA curve is significantly smaller than Z^6.

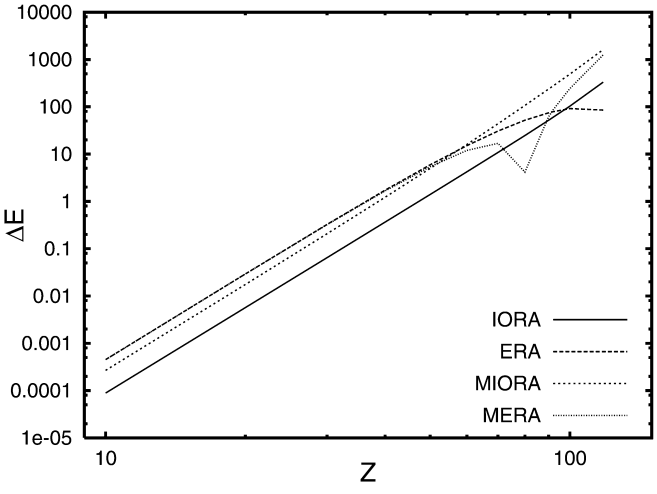

Fig. 2. A logarithmic plot of the difference between the quasi-relativistic and the corresponding Dirac energies for the one-electron $1s_{1/2}$ state as a function of nuclear charge

7.3 MIORA and MERA

The IORA and the ERA Hamiltonians both contain spin–orbit-dependent terms in the Hamiltonian and in the metric. The simplest approximation to the IORA and ERA models that does not have any spin-dependent terms in the metric is obtained by separating the $\hat{Y}$ operator into one term that is proportional to the nonrelativistic kinetic-energy operator $\hat{T}$, which is spin-independent, and into another less significant term, $\hat{B}$, that contains the spin–orbit coupling contributions in Eq. (15). The $\hat{B}$ operator in the metric can then be ignored. These equations are denoted MIORA-1 and MERA-1 models. In the MIORA-2 and MERA-2 models only the spin–orbit contribution to the $\hat{B}$ term in the metric is omitted. For the systems studied, the MERA-2 and IORA-2 Hamiltonians yield the ERA and IORA energies, respectively. The MIORA and MERA models are good starting points for the derivation of scalar-relativistic Hamiltonians that provide an easy way of considering spin–orbit effects by applying PT or configuration interaction. By omitting the spin–orbit contribution to the $2\hat{A} + \hat{B} + \hat{X}$ operator of the ERA model one obtains a one-component scalar-relativistic ERA model (SERA). The SERA Hamiltonian is an

economical one-component model that could replace the popular scalar ZORA approach.

The one-electron energies obtained using the MIORA-1 and MERA-1 methods are given in Table 3. The scaling factor $\gamma = 1$ was employed. In Fig. 2, the overall slope for the MIORA-1 and MERA-1 curves is 6; the MIORA-1 and the MERA-1 models are also correct up to $\alpha^2 Z^4$, but with a larger prefactor than for the IORA and ERA models. Note that the error of the MERA-1 model changes sign at about Hg^{79+}, which is seen in Fig. 2 as a dip in the MERA-1 curve. For one-electron atoms, γ can be adjusted until the MERA-1 and the Dirac energies agree. Since these γ values are not necessarily appropriate for many-electron systems, they are not discussed further here.

7.4. IORA + PT and ERA + PT

As shown in Sect. 5, two-component relativistic Hamiltonians such as IORA and ERA can be used as a zeroth-order approximation to the Dirac Hamiltonian. The operator difference between the two-component and the fully relativistic equations can be used as a perturbation operator and the corresponding energy difference can be considered by using a direct PT approach. The first-order PT corrections to the quasi-relativistic energies obtained with the IORA and the ERA Hamiltonian as the zeroth-order approximation to the Dirac equation are given in Table 1 and 2, respectively.

For the heaviest systems, the deviations between the Dirac energies and the total first-order PT energies are reduced by more than 1 order of magnitude, whereas for the lighter systems, the improvement due to the perturbation treatment is even a few of orders of magnitude. The difference between the total energies obtained at the IORA + PT level and the fully relativistic Dirac energies (ΔE) are plotted in Fig. 3 as a function of the nuclear charge. The same graph for the ERA + PT calculations is also shown.

As seen in Fig. 3, on a logarithmic scale the IORA + PT energy curve is linear with a slope of 10 implying that the IORA + PT energies are correct to order $\alpha^6 Z^8$. The corresponding curve for the ERA + PT energies is linear for small Z values but for heavier systems it is bent. The slope of the linear part is about 8; for lighter elements, the ERA + PT energies seems to be accurate up to the order $\alpha^4 Z^6$, whereas the discrepancy between the ERA + PT and the Dirac energies for the heavier systems is smaller than one would expect from an extrapolation of the $\alpha^4 Z^6$ line.

7.5. Optimized ERA

The ansatz used in the construction of the ERA Hamiltonian has one adjustable parameter, namely the scaling factor γ in the denominator of the exponent of the ansatz function in Eq. (7). Since $\gamma = 1$ yields at the nucleus the same first derivative of the ansatz function with respect to r as with the ZORA ansatz, this value for γ was used in the calculations presented earlier; however, γ can be adjusted rather freely. Optimal γ values can be obtained by minimizing the quasi-relativistic energy with respect to γ. Note that γ is not very significant for the overall wave function. It mainly defines the relation between the large and the small components at the vicinity of the nucleus, whereas at larger distances from the nucleus it affects the wave function only indirectly.

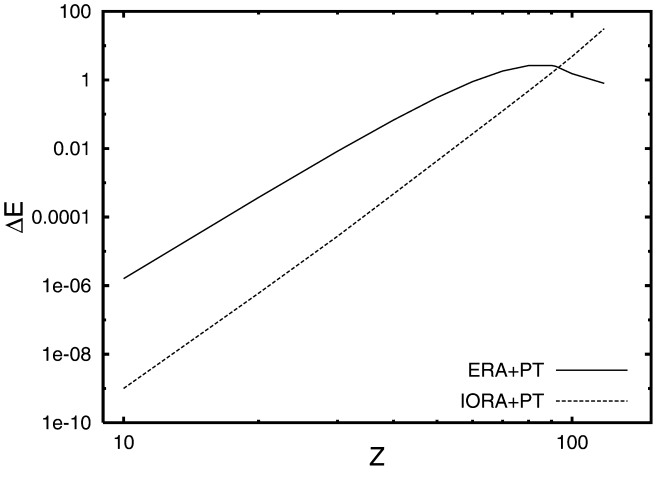

Fig. 3. The difference between the Dirac energy and the ERA + PT and IORA + PT energies, respectively, calculated as a function of nuclear charge

Table 3. The quasi-relativistic total energies (hartrees) for the lowest 1s state of one-electron atoms calculated at the metric modified IORA (MIORA-1) and metric modified ERA (MERA-1) levels. The energies are compared to the Dirac energies

Atom	E(MIORA-1)	Difference[a]	E(MERA-1)	Difference[b]
H	−0.500006657	0.0000000	−0.500006657	0.0000000
Ne^{9+}	−50.0664742	−0.0002678	−50.0671935	0.0004514
Ca^{19+}	−201.0590174	−0.0175059	−201.1056833	0.0291599
Zn^{29+}	−455.3182803	−0.2066268	−455.8479331	0.3230260
Zr^{39+}	−816.5873467	−1.2201512	−819.4761585	1.6686607
Sn^{49+}	−1289.6686470	−4.9575089	−1300.0174972	5.3913413
Nd^{59+}	−1879.7295502	−15.9528057	−1907.6166612	11.9343053
Yb^{69+}	−2591.1000119	−43.7465530	−2651.7135077	16.8669429
Hg^{79+}	−3425.5769377	−106.6152130	−3536.3559220	4.1637713
Th^{89+}	−4380.6590672	−237.0985871	−4556.0924249	−61.6652294
U^{91+}	−4585.5550537	−275.6429694	−4775.0432884	−86.1547347
Fm^{99+}	−5448.5425656	−490.6528187	−5695.5992208	−243.5961635
118^{117+}	−7612.6000344	−1618.0272897	−7979.3257421	−1251.3015821

[a] E(Dirac)-E(MIORA-1)
[b] E(Dirac)-E(MERA-1)

The accuracy of the quasi-relativistic energies and the first-order perturbation-energy corrections were studied by performing ERA and ERA + PT calculations on the two lowest $s_{1/2}$ states of U^{91+} using a few values for γ. The results of the ERA and ERA + PT calculations are summarized in Figs. 4 and 5, respectively. The difference between the ERA energy and the Dirac energy decreases with increasing γ. The smallest value for the energy difference was obtained with $\gamma = 1.40$. An analogous study at the ERA + PT level shows a similar trend; however, at the ERA + PT level the optimal γ value is 1.24.

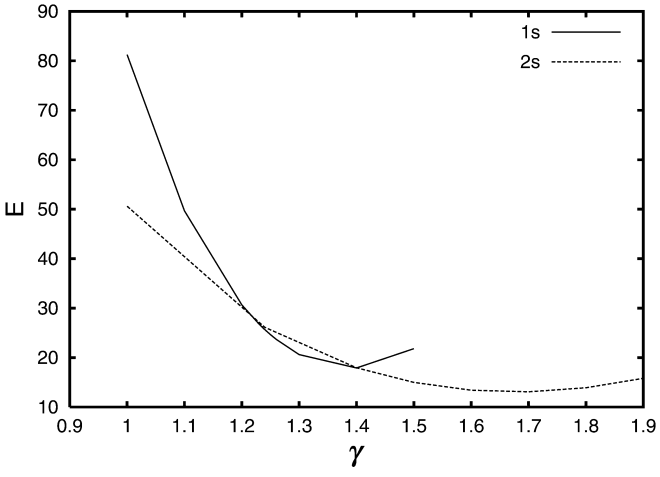

Fig. 4. The difference between the ERA and the Dirac energies for the $1s_{1/2}$ and the $2s_{1/2}$ states of U^{91+} as a function of the scaling factor γ

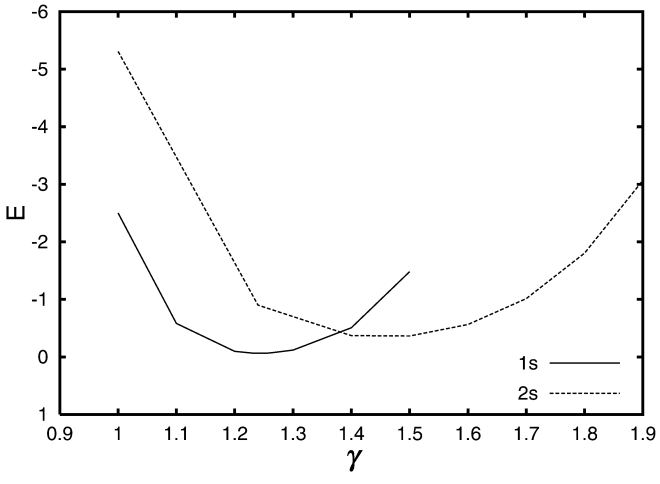

Fig. 5. The difference between the ERA + PT and the Dirac energies for the $1s_{1/2}$ and the $2s_{1/2}$ states of U^{91+} as a function of the scaling factor γ

A similar study for the first excited s state shows that at the ERA level, the optimal γ value of 1.7 provides a quasi-relativistic energy that is about a factor of 4 closer to the Dirac energy than when the default γ value of 1.0 is used. The optimal γ value obtained in the ERA + PT calculations on the $2s_{1/2}$ state of U^{91+} is about 1.5 and for this γ value the total ERA + PT energy is a factor of 15 closer to the exact Dirac energy than obtained with $\gamma = 1$. The results of the calculations on the $2s_{1/2}$ state of U^{91+} are summarized in Figs. 4 and 5. This study on U^{91+} shows that the optimal γ value seems to be always larger than 1. The optimal γ is also state- and model-dependent. At the ERA level, the optimal γ value is significantly larger than the γ value that yields the best ERA + PT energy. The reason for this is probably error compensation which is more significant for the less accurate ERA model than for the ERA + PT model. The ERA + PT calculations on U^{91+} with the optimal γ value almost reproduce the Dirac energy.

The energies of the ERA and ERA + PT calculations on the four lowest $s_{1/2}$ states of U^{91+} are compared to the exact results in Table 4. In the calculations, γ values of 1.0 and 1.24 were employed. The errors of the ERA energies were reduced by about a factor of 2 when $\gamma = 1.24$ was used. In the ERA + PT calculations, the improvements obtained by using the slightly larger γ value varied between a factor of 4 and a factor of 40 for the different states. Interestingly, larger improvements of the energies were obtained for the lower states with larger errors in the ERA energies. When one uses a γ value of 1.24, the absolute deviation between the ERA + PT energy and the exact results is of the same order of magnitude for all the states considered in Table 4.

The optimal γ values for the $1s_{1/2}$ states of one-electron atoms calculated at the ERA and the ERA + PT levels are shown in Fig. 6. As seen in Fig. 6, the optimal γ value for the ERA calculations are for all Z values larger than the γ value that provides the best ERA + PT energies. At the ERA level, γ increases approximately quadratically with decreasing nuclear charge. At the ERA + PT level, the optimal γ increases linearly with decreasing nuclear charge. For large Z values, γ approaches 1.

Table 4. The ERA energies (hartrees) of the four lowest s states of U^{91+} calculated using the scaling factors γ of 1.0 and 1.24, respectively and the corresponding first-order perturbation-energy correction. The energies are compared to the exact Dirac energies

[a] E(Dirac)-E(ERA)
[b] E(Dirac)-E(ERA + PT)

γ	State	E(ERA)	Difference[a]	E(PT)	Difference[b]
1.00	1s	−4939.9511031	78.7530800	81.2539373	−2.5008573
1.00	2s	−1308.0147730	50.6188827	55.9291894	−5.3103067
1.00	3s	−557.4653759	18.3720341	20.4902966	−2.1182625
1.00	4s	−303.3423060	8.0844619	9.0074174	−0.9229554
1.24	1s	−4886.8203383	25.6223152	25.6854565	−0.0631412
1.24	2s	−1283.5268558	26.1309655	27.0308256	−0.8998601
1.24	3s	−549.0364689	9.9431271	10.3443729	−0.4012458
1.24	4s	−299.7122445	4.4544004	4.6329240	−0.1785236

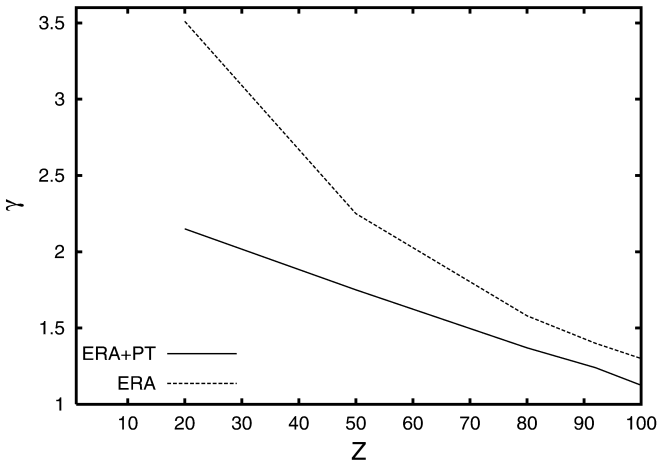

Fig. 6. The optimal scaling factor γ as a function of the nuclear charge for the one-electron $1s_{1/2}$ state calculated at the ERA and ERA + PT levels, respectively

In this study, only one-electron states have been considered. It is of course also possible to find optimal γ values for many-electron atoms. The optimal γ value for the atom would then be a compromise between the optimal γ values for each one-electron state. The optimal atomic γ values define a unique two-component optimized ERA model which could also be used in molecular calculations.

8 Summary

In this work, a method to derive general two-component relativistic Hamiltonians has been presented. The Dirac equation has been reformulated in such a way that two-component relativistic Hamiltonians can be identified as the zeroth-order approximation to the Dirac Hamiltonian. The operator difference between the two-component relativistic and the Dirac Hamiltonians can be treated as the perturbation operator in a direct PT scheme. The present approach is a straightforward method to determine the first-order relativistic perturbation-energy corrections to quasi-relativistic energies.

A couple of new two-component relativistic Hamiltonians have been proposed. The calculations show that the energies obtained with the present two-component relativistic Hamiltonians are in fairly good agreement with the corresponding Dirac energies. The discrepancy between the quasi-relativistic and the Dirac energies scales with $\alpha^4 Z^6$, where Z is the nuclear charge and α is the fine-structure constant.

The energy corrections obtained from first-order PT cover even for the heaviest one-electron atoms more than 90% of the difference between the energies obtained at the quasi-relativistic and the Dirac levels. The discrepancy between the Dirac energies and the energies of the two-component relativistic calculations corrected with the first-order perturbation energies scales for small Z values with $\alpha^6 Z^8$–$\alpha^8 Z^{10}$, depending on the zeroth-order Hamiltonian. By introducing optimized values for the scaling factor γ of the ERA model, significantly improved quasi-relativistic energies can be obtained.

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