Connection between the regular approximation and the normalized elimination of the small component in relativistic quantum theory

Michael Filatov[a] and Dieter Cremer
Department of Theoretical Chemistry, Göteborg University, Kemigården 3, S-41296 Göteborg, Sweden

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The regular approximation to the normalized elimination of the small component (NESC) in the modified Dirac equation has been developed and presented in matrix form. The matrix form of the infinite-order regular approximation (IORA) expressions, obtained in [Filatov and Cremer, J. Chem. Phys. **118**, 6741 (2003)] using the resolution of the identity, is the exact matrix representation and corresponds to the zeroth-order regular approximation to NESC (NESC-ZORA). Because IORA (=NESC-ZORA) is a variationally stable method, it was used as a suitable starting point for the development of the second-order regular approximation to NESC (NESC-SORA). As shown for hydrogenlike ions, NESC-SORA energies are closer to the exact Dirac energies than the energies from the fifth-order Douglas–Kroll approximation, which is much more computationally demanding than NESC-SORA. For the application of IORA (=NESC-ZORA) and NESC-SORA to many-electron systems, the number of the two-electron integrals that need to be evaluated (identical to the number of the two-electron integrals of a full Dirac–Hartree–Fock calculation) was drastically reduced by using the resolution of the identity technique. An approximation was derived, which requires only the two-electron integrals of a nonrelativistic calculation. The accuracy of this approach was demonstrated for heliumlike ions. The total energy based on the approximate integrals deviates from the energy calculated with the exact integrals by less than 5×10^{-9} hartree units. NESC-ZORA and NESC-SORA can easily be implemented in any nonrelativistic quantum chemical program. Their application is comparable in cost with that of nonrelativistic methods. The methods can be run with density functional theory and any wave function method. NESC-SORA has the advantage that it does not imply a picture change. © *2005 American Institute of Physics*.
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I. INTRODUCTION

For the majority of all elements of the periodic table, the inclusion of relativistic effects is important for obtaining accurate quantum mechanical descriptions of their properties either in atomic or molecular form.[1–3] This is especially true for compounds containing heavy elements, where relativity makes sizable (sometimes even dominating) contributions not only with regard to their physical properties,[1,4,5] such as magnetic response properties, but also with regard to chemical bonding and chemical reactivity.[1–3] Although substantial progress has been made in the field of rigorous four-component relativistic calculations based on the Dirac Hamiltonian,[5,6] these calculations still remain prohibitively costly even for medium-sized molecular systems. Therefore, there is a growing demand for simple yet accurate approximate relativistic all-electron methods that can be easily installed within the existing quantum-chemical program packages and that can be used routinely in calculations on larger, chemically interesting molecules.

The all-electron methods derived from the so-called regular approximation to the exact relativistic Hamiltonian[7–12] furnish perhaps the most promising tools in relativistic quantum chemistry. The starting point for deriving the regular approximation is the assumption of a strong electron binding potential in such a way that the explicit energy dependence on the relativistic transformation operators can be disregarded and instead be taken into account in a perturbational fashion.[8–12] Because in atoms and molecules, the electrons move in the strong Coulomb potential of the nuclei, this assumption seems to be well suited for atomic and molecular calculations. The development of the regular approximation is made usually in terms of operators rather than matrices.[8–10] This route leads to an algebraic expression for the regular Hamiltonian operator, which contains the full atomic or molecular potential in the denominator.[8–10] Therefore, for a long time, any wave function based quantum-chemical description using the relativistic Hamiltonian in the regular approximation required tedious numeric quadratures[13] as the only way for the evaluation of needed matrix elements over basis set functions.

A more efficient alternative was provided by us in form of the matrix ZORA (zeroth-order regular approximation) and matrix IORA (infinite-order regular approximation) approaches.[12,14,15] For these methods, any numeric quadratures are avoided by the analytic evaluation of the matrix elements of the regular Hamiltonian utilizing the resolution of the identity (RI) as defined by a given finite basis set. This leads to a simple and efficient algorithm, which can be actu-

[a]Electronic mail: filatov@theoc.gu.se

ally used within the context of both density functional theory and wave function theory (WFT). On first sight, one may consider the use of the RI as a useful mathematical trick rather than as a methodological extension of the regular approximation with a specific physical meaning. In this work, however, we will demonstrate that, if the development of the regular approximation is carried out within the matrix representation of the exact relativistic equations, modified according to Dyall,[16] the same analytic formulas can be obtained for the matrix ZORA and matrix IORA as published in our previous work without requiring at any stage the use of the RI.

It is the primary objective of the present paper to develop the connection between the regular approximation and the method of the normalized elimination of the small component[16] (NESC) from the Dirac equation.[17] The NESC method corresponds to the projection of the Dirac Hamiltonian onto a set of positive-energy (electronic) states, which guarantees its variational stability.[16] The solution of the NESC method is the same as that of the Dirac equation.[18] Thus, connecting the regular approximation and NESC means that the regular approximation is directly connected to the Dirac equation. An advantage of NESC is that this method is formulated in matrix form,[16] which permits the formulation of the regular approximation within WFT, i.e., in a form perfectly suited for atomic and molecular calculations with finite basis sets.

The current paper comprises beside the Introduction three additional sections: In Sec. II, the NESC method is briefly described. The relationship between the regular approximation and NESC is presented in Sec. III for the case of a single electron whereas it is extended to the many-electron case in Sec. IV. NESC-ZORA and NESC-SORA (second-order regular approximation) emerge out of this work, which are applied to a series of hydrogenlike and heliumlike atomic ions. Results of these calculations are compared with the exact relativistic values. Finally, Sec. IV describes an algorithm which largely simplifies the calculation of relativistically-corrected two-electron integrals.

II. NORMALIZED ELIMINATION OF THE SMALL COMPONENT

For a single electron moving in the potential field $V(\mathbf{r})$, the Dirac equation, modified according to Dyall, reads[16]

$$\hat{T}\Phi_L + V(\mathbf{r})\Psi_L = E\Psi_L, \tag{1a}$$

$$\hat{T}\Psi_L + \frac{1}{4m^2c^2}(\sigma\cdot\mathbf{p})[V(\mathbf{r}) - E](\sigma\cdot\mathbf{p})\Phi_L = \hat{T}\Phi_L, \tag{1b}$$

where $\hat{T}$ and $\mathbf{p}$ are the usual kinetic energy and linear momentum operators, m is the electron mass, c velocity of light, and σ is the vector of Pauli matrices.[19] The function Ψ_L is the large component of the Dirac wave function and the pseudolarge component Φ_L is connected to the small component Ψ_S of the Dirac wave function via Eq. (2),[16]

$$\Psi_S = \frac{(\sigma\cdot\mathbf{p})}{2mc}\Phi_L. \tag{2}$$

With the use of Eq. (2), the so-called *kinetic balance* condition[20] is embedded into the modified Dirac equation (1). Therefore, the same basis set $|\chi\rangle$ can be used to expand the large and pseudolarge components of the modified Dirac wave function, which leads to the following set of matrix equations for the expansion coefficients, denoted (following Dyall) **A** and **B**, respectively:[16]

$$\mathbf{TB} + \mathbf{VA} = \mathbf{SAE}, \tag{3a}$$

$$\mathbf{TA} + (\mathbf{W}_0 - \mathbf{T})\mathbf{B} = \frac{1}{2mc^2}\mathbf{TBE}. \tag{3b}$$

In Eq. (3), **A** and **B** are the matrices of the expansion coefficients for the large and pseudolarge components, **T** and **V** are the matrices of the kinetic and of the potential energy operators, respectively, **S** is the overlap matrix, and $\mathbf{W}_0$ is the matrix of the operator $(\sigma\cdot\mathbf{p})V(\mathbf{r})(\sigma\cdot\mathbf{p})/(4m^2c^2)$, used in our previous works.[14,15]

The elimination of the small component in Eq. (3) is achieved by the use of a general nonunitary transformation matrix **U**, which connects the expansion coefficients matrices **A** and **B** via Eq. (4),

$$\mathbf{B} = \mathbf{UA}. \tag{4}$$

By requiring that the proper normalization of the modified Dirac wave function is retained, i.e.,

$$\mathbf{A}^\dagger\mathbf{SA} + \frac{1}{2mc^2}\mathbf{B}^\dagger\mathbf{TB} = \mathbf{I}, \tag{5}$$

one obtains the NESC equation (6)

$$(\tilde{\mathbf{T}} + \tilde{\mathbf{V}})\mathbf{A} = \tilde{\mathbf{S}}\mathbf{AE}, \tag{6}$$

where the modified kinetic energy, potential energy, and overlap matrices are defined in Eq. (7),

$$\tilde{\mathbf{T}} = \mathbf{U}^\dagger\mathbf{T} + \mathbf{TU} - \mathbf{U}^\dagger\mathbf{TU}, \tag{7a}$$

$$\tilde{\mathbf{V}} = \mathbf{V} + \mathbf{U}^\dagger\mathbf{W}_0\mathbf{U}, \tag{7b}$$

$$\tilde{\mathbf{S}} = \mathbf{S} + \frac{1}{2mc^2}\mathbf{U}^\dagger\mathbf{TU}. \tag{7c}$$

The matrix **U** satisfies Eq. (8)

$$\begin{aligned}\mathbf{U} &= \mathbf{T}^{-1}\left(\tilde{\mathbf{T}} + \mathbf{U}^\dagger\mathbf{W}_0\mathbf{U} - \frac{1}{2mc^2}\mathbf{U}^\dagger\mathbf{TUAEA}^{-1}\right)\\ &= \mathbf{T}^{-1}\left(\tilde{\mathbf{T}} + \mathbf{U}^\dagger\mathbf{W}_0\mathbf{U} - \frac{1}{2mc^2}\mathbf{U}^\dagger\mathbf{TU}\tilde{\mathbf{S}}^{-1}\mathbf{H}\right),\end{aligned} \tag{8}$$

where $\mathbf{H}=\tilde{\mathbf{T}}+\tilde{\mathbf{V}}$ and the relationships (9a) and (9b) for the eigenvectors **A** of a matrix **H** normalized on a metric $\tilde{\mathbf{S}}$ were used in the second line of Eq. (8),

$$\mathbf{A}^{-1} = \mathbf{A}^\dagger\tilde{\mathbf{S}}, \tag{9a}$$

$$\mathbf{H} = \tilde{\mathbf{S}}\mathbf{AEA}^\dagger\tilde{\mathbf{S}}. \tag{9b}$$

The system of Eqs. (6) and (8) is solved iteratively starting with some suitable guess for **U**.

It has been shown[16] that the NESC method corresponds to the projection of the Dirac Hamiltonian onto a set of positive-energy eigenstates, which guarantees its variational stability. In this respect, the NESC method represents a viable alternative to other techniques (e.g., the Douglas–Kroll approach[21]) that project the full set of solutions of the Dirac equation onto the manifold of positive-energy (electronic) states. However, the metric $\tilde{\mathbf{S}}$ in Eq. (6) varies from iteration to iteration so that, in the many-electron case, the two-electron integrals must be tediously recalculated at each iteration.[16]

III. REGULAR APPROXIMATION TO NESC

For the purpose of simplifying the solution of the NESC equations, we assume that the dependence of matrix $\mathbf{U}$ on the energy eigenvalues $\mathbf{E}$ is weak and that the last term on the right-hand side of Eq. (8) can be neglected. After some algebra, the following equation for matrix $\mathbf{U}^{(0)}$ is obtained with these assumptions:

$$(\mathbf{U}^{(0)})^{\dagger}\mathbf{T} - (\mathbf{U}^{(0)})^{\dagger}\mathbf{T}\mathbf{U}^{(0)} + (\mathbf{U}^{(0)})^{\dagger}\mathbf{W}_0\mathbf{U}^{(0)} = 0, \tag{10}$$

where the superscript 0 denotes the zeroth-order approximation of $\mathbf{U}$ (with respect to the energy eigenvalues). Equation (10) is solved by $\mathbf{U}^{(0)}$ in Eq. (11),

$$\mathbf{U}^{(0)} = (\mathbf{T} - \mathbf{W}_0)^{-1}\mathbf{T}. \tag{11}$$

Substitution of Eq. (11) into the NESC equation (6) yields Eq. (12) as the zeroth-order approximation to NESC,

$$[\mathbf{T}(\mathbf{T} - \mathbf{W}_0)^{-1}\mathbf{T} + \mathbf{V}]\mathbf{A} = \left[\mathbf{S} + \frac{1}{2mc^2}\mathbf{T}(\mathbf{T} - \mathbf{W}_0)^{-1}\mathbf{T}(\mathbf{T} - \mathbf{W}_0)^{-1}\mathbf{T}\right]\mathbf{A}\mathbf{E}. \tag{12}$$

Using the fact that for two symmetric matrices $\mathbf{X}$ and $\mathbf{Y}$ the following relationship holds:[11]

$$(\mathbf{X}^{-1} - \mathbf{Y}^{-1})^{-1} = \mathbf{Y}(\mathbf{Y} - \mathbf{X})^{-1}\mathbf{Y} - \mathbf{Y}, \tag{13}$$

Eq. (12) can be transformed to Eq. (14),

$$(\mathbf{T} + \mathbf{W} + \mathbf{V})\mathbf{A} = \left[\mathbf{S} + \frac{1}{2mc^2}(\mathbf{T} + 2\mathbf{W} + \mathbf{W}\mathbf{T}^{-1}\mathbf{W})\right]\mathbf{A}\mathbf{E}, \tag{14}$$

where matrix $\mathbf{W}$ is the solution of Eq. (15):

$$\mathbf{W} = \mathbf{W}_0 + \mathbf{W}_0\mathbf{T}^{-1}\mathbf{W}. \tag{15}$$

In Eq. (14), the IORA matrix equation derived in our previous works[14,15] utilizing the RI can be easily recognized. This proofs that (a) the use of the RI is actually not needed and (b) that the previously derived matrix IORA equation is the exact lowest-order regular approximation to the matrix Dirac equation.

It is interesting to see what would happen if one started from the modified Dirac equation (3) directly, rather than from the NESC equation (6). In the spirit of the regular approximation,[8–12] the right-hand side of Eq. (3b), which leads to the energy dependence of the operator $\mathbf{U}$, Eq. (4), is set to zero. Immediately, one arrives at Eq. (11) for the lowest-order regularly approximated operator $\mathbf{U}^{(0)}$, which upon substituting into Eq. (3a) yields Eq. (16),

$$[\mathbf{T}(\mathbf{T} - \mathbf{W}_0)^{-1}\mathbf{T} + \mathbf{V}]\mathbf{A} = (\mathbf{T} + \mathbf{W} + \mathbf{V})\mathbf{A} = \mathbf{S}\mathbf{A}\mathbf{E}. \tag{16}$$

Equation (16) is nothing else than the matrix ZORA equation. One must, however, realize that the large component eigenvectors $\mathbf{A}$ are normalized by the condition (5). If this constraint is lifted, the large component will be improperly normalized on the nonrelativistic metric. In this respect, the matrix ZORA equation is the lowest-order regular approximation to the equation for the unnormalized elimination of the small component, henceforth called UESC-ZORA. In the IORA equation (14), the proper normalization for the large-component wave function is approximated on the right-hand side. Therefore, this is the lowest-order approximation to the normalized theory.

Let us now consider the iterative solution of Eqs. (6) and (8) using Eq. (11) as starting guess. The zeroth-order Hamiltonian $\mathbf{H}^{(0)}$ and the zeroth-order metric $\tilde{\mathbf{S}}^{(0)}$ are given by the terms in parentheses on the left-hand side (lhs) and the right-hand side (rhs) of Eq. (12), respectively. From Eq. (8) it follows that the next approximation to the operator $\mathbf{U}$ is

$$\mathbf{U}^{(1)} = \mathbf{T}^{-1}\left[\mathbf{T}(\mathbf{T} - \mathbf{W}_0)^{-1}\mathbf{T} - \frac{1}{2mc^2}\mathbf{T}(\mathbf{T} - \mathbf{W}_0)^{-1}\mathbf{T}(\mathbf{T} - \mathbf{W}_0)^{-1}\mathbf{T}(\tilde{\mathbf{S}}^{(0)})^{-1}\mathbf{H}^{(0)}\right] = \mathbf{U}^{(0)} - \frac{1}{2mc^2}\mathbf{U}^{(0)}\mathbf{U}^{(0)}(\tilde{\mathbf{S}}^{(0)})^{-1}\mathbf{H}^{(0)}, \tag{17}$$

where

$$\mathbf{H}^{(0)} = \mathbf{T}(\mathbf{T} - \mathbf{W}_0)^{-1}\mathbf{T} + \mathbf{V} \tag{18}$$

and

$$\tilde{\mathbf{S}}^{(0)} = \mathbf{S} + \frac{1}{2mc^2}(\mathbf{U}^{(0)})^{\dagger}\mathbf{T}\mathbf{U}^{(0)}. \tag{19}$$

Therefore, the next approximation to the NESC Hamiltonian is

$$\mathbf{H}^{(2)} = \mathbf{H}^{(0)} - \frac{1}{(2mc^2)^2}\mathbf{H}^{(0)}(\tilde{\mathbf{S}}^{(0)})^{-1}(\mathbf{U}^{(0)})^{\dagger} \times \mathbf{T}(\mathbf{T} - \mathbf{W}_0)^{-1}\mathbf{T}\mathbf{U}^{(0)}(\tilde{\mathbf{S}}^{(0)})^{-1}\mathbf{H}^{(0)}. \tag{20}$$

The superscript 2, used in Eq. (20), emphasizes that the Hamiltonian matrix $\mathbf{H}^{(2)}$ has second-order dependence on the lowest-order Hamiltonian $\mathbf{H}^{(0)}$ and, consequently, on the eigenvalues $\mathbf{E}^{(0)}$. For the new metric, one has Eq. (21),

$$\tilde{\mathbf{S}}^{(2)} = \tilde{\mathbf{S}}^{(0)} - \frac{1}{(2mc^2)^2}\mathbf{H}^{(0)}(\tilde{\mathbf{S}}^{(0)})^{-1}(\mathbf{U}^{(0)})^{\dagger}\mathbf{T}(\mathbf{T} - \mathbf{W}_0)^{-1} \times \mathbf{T}\mathbf{U}^{(0)} - \frac{1}{(2mc^2)^2}(\mathbf{U}^{(0)})^{\dagger}\mathbf{T}(\mathbf{T} - \mathbf{W}_0)^{-1}\mathbf{T}\mathbf{U}^{(0)} \times (\tilde{\mathbf{S}}^{(0)})^{-1}\mathbf{H}^{(0)} + \frac{1}{(2mc^2)^3}\mathbf{H}^{(0)} \times (\tilde{\mathbf{S}}^{(0)})^{-1}(\mathbf{U}^{(0)})^{\dagger}(\mathbf{U}^{(0)})^{\dagger}\mathbf{T}\mathbf{U}^{(0)}\mathbf{U}^{(0)}(\tilde{\mathbf{S}}^{(0)})^{-1}\mathbf{H}^{(0)}, \tag{21}$$

TABLE I. Ground state energies (in hartree units) of hydrogenlike atomic ions calculated with different quasirelativistic methods and compared with the exact (Dirac) energies.

Method	$Z=20$[a]	40	60	80	100	120
Dirac equation	−201.076 523	−817.807 498	−1895.682 36	−3532.192 15	−5939.1984	−9 710.7835
ZORA	−202.158 829	−836.011 368	−1996.450 87	−3898.869 16	−7054.8079	−13 096.9617
IORA	−201.082 194	−818.171 957	−1899.900 00	−3536.901 02	−6042.5850	−10 089.4142
DK1[b]	−201.341 494	−823.894 221	−1934.202 84	−3686.448 68	−6472.4026	−12 132.6799
NESC-SORA	−201.076 522	−817.807 633	−1895.689 72	−3532.312 24	−5940.2749	−9 718.0099
DK2[c]	−201.072 538	−817.615 772	−1893.897 64	−3523.324 84	−5906.1918	−9 694.0960
DK5[d]	−201.076 523	−817.808 095	−1895.702 82	−3532.461 47	−5941.5285	−9 730.9684
DK6[e]	−201.076 52	−817.807 38	−1895.676 84	−3532.101 21	−5938.3145	−9 703.6645

[a]Nuclear charge.
[b]First-order Douglas–Kroll method (Ref. 22).
[c]Second-order Douglas–Kroll method (Ref. 22).
[d]Fifth-order Douglas–Kroll method (Ref. 22).
[e]Sixth-order Douglas–Kroll method (Ref. 23).

which again has second-order dependence on the zeroth-order Hamiltonian. Consequently, iterating the NESC equations (6) and (8) once, leads consistently to the second-order (in terms of the zeroth-order eigenvalues) correction to the Hamiltonian and wave function metric. Therefore, the method where $\mathbf{H}^{(2)}$ and $\tilde{\mathbf{S}}^{(2)}$ are used represents the second-order regular approximation to the NESC equation, henceforth called NESC-SORA for brevity.

The recurrent iteration of Eqs. (6) and (8) can be continued, which will ultimately lead to the exact solution of the NESC equations. This, however, may not be necessary, because already at the NESC-SORA level results of high accuracy are obtained. Table I summarizes relativistic energies for a series of hydrogenlike atomic ions calculated with the ZORA, IORA, and NESC-SORA and compares these energies with the exact solutions of the Dirac equation and with the results obtained with the Douglas–Kroll (DK) approximation.[21–23] For the calculations, a basis set of 50 primitive *s*-type Gaussian functions taken from the work of Wolf *et al.*[22] was employed.

Calculated IORA energies (which can be alternatively considered as being determined with the zeroth-order regular approximation to NESC, i.e., NESC-ZORA) and NESC-SORA energies show rapid and smooth convergence from below to the exact Dirac energies. The convergence from below is consistent with the fact, proven by Dyall,[16] that, for any trial wave function, NESC provides a lower bound to the exact (Dirac) energy. In terms of numerical accuracy, IORA performs much better than the lowest-order DK method, DK1. In turn, NESC-SORA performs better than the next Douglas–Kroll approximation DK2, which is the method of comparable computational complexity. In fact, NESC-SORA outperforms the fifth-order DK method DK5, in terms of numerical accuracy and performs as good as the much more demanding DK6 method. Note that for the construction of the Hamiltonian operator matrix in DK5 and DK6 888 and 7832 matrix multiplications are required,[23] which makes the implementation of these methods a nontrivial and tedious task. Furthermore, the Douglas–Kroll approach suffers from erratic (oscillating) and slow convergence[22,23] to the exact energy whereas the convergence of the regular approximations to NESC is rapid and monotonic.[16]

A serious disadvantage of the ZORA and IORA methods is their lack of gauge invariance.[8–11] If a constant shift Δ is added to the potential,

$$V_\Delta(\mathbf{r}) = V(\mathbf{r}) + \Delta, \tag{22}$$

then the eigenvalues of a gauge invariant method should be shifted by exactly the same amount Δ. For IORA, the gauge shift error (GSE) is[10]

$$E_0^{\mathrm{IORA}} - E_\Delta^{\mathrm{IORA}} + \Delta \approx -\frac{(E_0^{\mathrm{IORA}})^2\Delta}{4m^2c^4}, \tag{23}$$

which is small compared to the gauge dependence of ZORA,[8,9]

$$E_0^{\mathrm{ZORA}} - E_\Delta^{\mathrm{ZORA}} + \Delta \approx \frac{E_0^{\mathrm{ZORA}}\Delta}{2mc^2}, \tag{24}$$

however, still large enough to induce a considerable distortion of the molecular geometry if the method is applied in molecular calculations.[11] The NESC-SORA method reduces the GSE further,

$$E_0^{\text{NESC-SORA}} - E_\Delta^{\text{NESC-SORA}} + \Delta \approx -\frac{(E_0^{\text{NESC-SORA}})^3\Delta}{8m^3c^6} \tag{25}$$

making it of order $O(c^{-6})$. This can be illustrated with the numeric values of GSE calculated for hydrogenlike fermium ($Z=100$) for the gauge shift $\Delta=-100$ hartree units. GSE of ZORA, obtained from the left-hand side of Eq. (24), amounts to 18.783 905 hartree units, GSE of IORA to 3.151 604 hartree units and GSE of NESC-SORA to 0.065 912 hartree units. This is really weak gauge dependence, which would not lead to noticeable distortions of molecular geometry.[11] However, even this weak gauge dependence can be eliminated completely with the use of the gauge-independence correction developed in our recent publication.[24]

IV. MANY-ELECTRON CASE

For a system of many electrons, the self-consistent field Kramers-restricted[25] NESC equation, which employs the Coulomb two-electron operator, reads[16]

$$(\tilde{\mathbf{T}} + \tilde{\mathbf{V}} + 2\tilde{\mathbf{J}} - \tilde{\mathbf{K}})\mathbf{A} = \tilde{\mathbf{S}}\mathbf{A}\mathbf{E}, \tag{26}$$

where the kinetic energy and the metric matrices $\tilde{\mathbf{T}}$ and $\tilde{\mathbf{S}}$ are defined in Eq. (7), the matrix $\tilde{\mathbf{V}}$ [see Eq. (7)] is calculated using the electron-nuclear attraction potential, and elements of the Coulomb and exchange matrices are given in Eq. (27),[16]

$$\tilde{J}_{\mu\nu} = \sum_{\kappa\lambda} (\tilde{\mu}\tilde{\nu}|\tilde{\kappa}\tilde{\lambda}) D_{\kappa\lambda}, \tag{27a}$$

$$\tilde{K}_{\mu\nu} = \sum_{\kappa\lambda} ((\tilde{\mu}\tilde{\lambda}|\tilde{\kappa}\tilde{\nu}) + (\tilde{\mu}\tilde{\bar{\kappa}}|\tilde{\bar{\lambda}}\tilde{\nu})) D_{\kappa\lambda}. \tag{27b}$$

In Eq. (27), **D** is the density matrix constructed from the eigenvectors of Eq. (26), the transformed two-electron integrals are given in Eq. (28), and the bar over the basis function symbol means that this is the time-reversal counterpart of the respective basis function,[25]

$$\begin{aligned}(\tilde{\mu}\tilde{\nu}|\tilde{\kappa}\tilde{\lambda}) = (\mu\nu|\kappa\lambda) + \frac{1}{4m^2c^2}\sum_{\tau\rho} (U^*_{\tau\mu}(\hat{\Pi}\tau\hat{\Pi}\rho|\kappa\lambda)U_{\rho\nu} \\ + U^*_{\tau\kappa}(\mu\nu|\hat{\Pi}\tau\hat{\Pi}\rho)U_{\rho\lambda}) + \frac{1}{16m^4c^4} \\ \times \sum_{\tau\rho}\sum_{\zeta\eta} U^*_{\tau\mu}U^*_{\zeta\kappa}(\hat{\Pi}\tau\hat{\Pi}\rho|\hat{\Pi}\zeta\hat{\Pi}\eta)U_{\rho\nu}U_{\eta\lambda}.\end{aligned} \tag{28}$$

In Eq. (28), the symbol $\hat{\Pi}$ stands for the operator $(\sigma\cdot\mathbf{p})$, and $U_{\mu\nu}$, etc., are elements of the matrix **U**, which connects the large and pseudolarge components of the modified Dirac wave function via. Eq. (4).

In the many-electron case, the matrix **U** satisfies the following equation:[16]

$$\begin{aligned}\left(\mathbf{T} - \frac{1}{4m^2c^2}\mathbf{K}^{LS}\right)\mathbf{U} = \left(\mathbf{I} - \frac{1}{2mc^2}\mathbf{U}^\dagger\mathbf{T}\mathbf{U}\tilde{\mathbf{S}}^{-1}\right)\tilde{\mathbf{F}} \\ - \left(\mathbf{V} + (2\mathbf{J}^{LL} - \mathbf{K}^{LL}) + \frac{1}{2m^2c^2}\mathbf{J}^{SL}\right),\end{aligned} \tag{29}$$

where $\tilde{\mathbf{F}}$ denotes the operator in parentheses on the left-hand side of Eq. (26), and the electron-electron interaction matrices $\mathbf{J}^{LL}$, $\mathbf{K}^{LL}$, $\mathbf{K}^{LS}$, and $\mathbf{J}^{SL}$ are defined in Eqs. (46) and (47) of Ref. 16 and are not reproduced here for reasons of brevity. Through the dependence on $\tilde{\mathbf{F}}$, the matrix **U** depends on the orbital energies and varies from iteration to iteration of the self-consistent field procedure. This leads to the necessity of recalculating the modified two-electron integrals at each iteration of the self-consistent field (SCF) cycle. In order to remove the energy dependence of **U**, Dyall considered a low order approximation to NESC with $\mathbf{U}=\mathbf{I}$.[26] However, this approximation occurred to be variationally unstable and was therefore abandoned.[26]

For the purpose of applying the regular approximation scheme, developed in the preceding section, we simplify the equation defining matrix **U** in the following way. Considering that Eq. (30) holds

$$\tilde{\mathbf{F}} = \tilde{\mathbf{T}} + \tilde{\mathbf{V}} + (2\mathbf{J}^{LL} - \mathbf{K}^{LL}) + O\left(\frac{1}{c^2}\right), \tag{30}$$

Eq. (29) can be transformed to Eq. (31),

$$\mathbf{U} = \mathbf{T}^{-1}\left(\tilde{\mathbf{T}} + \mathbf{U}^\dagger\mathbf{W}_0\mathbf{U} - \frac{1}{2mc^2}\mathbf{U}^\dagger\mathbf{T}\mathbf{U}\tilde{\mathbf{S}}^{-1}\mathbf{H}\right) + O\left(\frac{1}{c^2}\right), \tag{31}$$

where the two-electron terms with the $O(c^{-2})$ dependence are placed outside the parentheses. If the latter terms are neglected, an equation identical to Eq. (8) results and all derivations undertaken in the preceding section can be applied to the set of Eqs. (26) and (31). The neglected two-electron terms of Eq. (31) make contributions of order $O(c^{-4})$ to both the Hamiltonian and wave function metric. Furthermore, these terms are much smaller in their magnitude than the one-electron terms of the same order in $1/c^2$. Hence, neglecting them will not introduce any significant error (see below).

If one wants to implement the IORA (=NESC-ZORA) method for the many-electron case, one will need to replace the matrix **U** in Eqs. (26)–(28) by the zeroth-order approximation $\mathbf{U}^{(0)}$. Note that one has to calculate only the electron-nuclear attraction potential to determine $\mathbf{U}^{(0)}$ according to Eq. (11). Implementation of NESC-SORA is achieved by the use of Eq. (17) for $\mathbf{U}^{(1)}$, which leads to Eqs. (20) and (21) for the one-electron part of the modified Fock operator $\tilde{\mathbf{F}}$ and the wave function metric, respectively.

The many-electron NESC-SORA algorithm described was programmed and tested by calculating the energies of a series of heliumlike atomic ions. These systems represent a stringent test for the approximations made because the relativistic correction to the electron-electron interaction energy is largest for the 1*s* electrons. Again, the basis set of 50 primitive Gaussian-type functions was used as before for the hydrogenlike ions. The reference data,[27,28] reported in Table II, were obtained by Dirac–Hartree–Fock (DHF) calculations that employed point charge nucleus for light elements ($Z=2$, 10, and 18) (Ref. 27) and a nucleus of finite size for heavier elements ($Z=30$ to 100).[28] In the NESC-SORA calculations, the extended nucleus is modeled by a Gaussian charge distribution with the nuclear radii taken from the compilation in Ref. 29.

The comparison reveals that the NESC-SORA approach performs fairly well and even for the heaviest element considered Fm^{98+} the deviation from the reference value is just ca. 0.1% of the relativistic correction to the total energy. This is a very good result considering the simplicity of the implementation of the computational scheme. Indeed, in the one-electron part of the Fock operator of NESC-SORA, no dependence on the electron-electron interaction is present and the wave function metric remains constant throughout the SCF calculation. The quality of the results confirms also that the assumption made in Eq. (31) is sufficiently accurate. Implementation of the one-electron part of NESC-SORA can be achieved with the use of the molecular one-electron integrals available routinely in standard nonrelativistic program codes.

TABLE II. Ground state energies (in hartree units) of heliumlike atomic ions calculated with different quasirelativistic methods and compared with the Dirac–Hartree–Fock (DHF) energies. See text for details on basis sets and nuclear models.

Z[a]	DHF[b]	NESC-SORA (full $2\overline{e}$ operator)	NESC-SORA (approximate $2\overline{e}$ operator)	NESC-SORA (nonrelativistic $2\overline{e}$ operator)
2	−2.861 813[c]	−2.861 813	−2.861 781	−2.861 895
10	−93.982 799[c]	−93.982 799	−93.976 746	−93.998 019
18	−314.200 163[c]	−314.200 165	−314.163 208	−314.293 251
30	−892.051 699[d]	−892.066 344	−891.890 331	−892.513 199
40	−1 609.845 54[d]	−1 609.868 35	−1 609.444 19	−1 610.956 50
50	−2 556.278 65[d]	−2 556.312 51	−2 555.470 81	−2 558.502 50
60	−3 750.477 22[d]	−3 750.534 88	−3 749.055 25	−3 754.455 41
70	−5 219.574 52[d]	−5 219.618 16	−5 217.222 31	−5 226.114 31
80	−7 002.382 84[d]	−7 002.701 04	−6 999.041 03	−7 012.916 13
90	−9 155.388 99[d]	−9 156.001 00	−9 150.642 48	−9 171.508 25
100	−11 763.908 4[d]	−11 766.362 8	−11 758.751 1	−11 789.421 9

[a]Nuclear charge.
[b]DHF results.
[c]From Ref. 27.
[d]From Ref. 28.

However, considerable computational complexity is caused by the calculation of the modified two-electron integrals.[16,26] The matrix $\mathbf{U}^{(1)}$ is constant during the iteration, which simplifies the calculation. Negative, however, is the necessity of calculating a large number of auxiliary integrals in Eq. (28) (see second and third terms on the rhs). These are the same integrals, which have to be calculated in standard DHF calculations.[16,26] Therefore, it means little saving in computational cost when approximating only the one-electron part of the many-electron Hamiltonian. The two-electron part has to be simplified as well.

It has to be stressed that the second and the third term on the rhs of Eq. (28) make significant contributions to the total energy of a heavy atom. If these integrals are neglected, thus making the computation of the two-electron part of the NESC-SORA Fock operator identical to that of the nonrelativistic case, the error for heavy ions will increase by an order of magnitude (see last column in Table II). Electron-electron repulsion is underestimated in this case, because the large-component wave function, approximated in NESC-SORA, is not normalized on the nonrelativistic metric and yields therefore,

$$\mathrm{tr}(\mathbf{DS}) < N, \tag{32}$$

where N is the number of electrons.

Inspection of Eq. (28) reveals that the third term on the rhs can be omitted without significant loss in accuracy because of its prefactor. Calculation of the integrals in the second term on the rhs of (28) can be simplified in the following way. Let us first make a spin-free approximation, replacing the $\hat{\Pi}$ operator in Eq. (28) with the linear momentum operator $\mathbf{p}$. Then, the integral $(\mathbf{p}\mu\cdot\mathbf{p}\nu|\kappa\lambda)$ can be represented according to Eq. (33),

$$\begin{aligned}(\mathbf{p}\mu\cdot\mathbf{p}\nu|\kappa\lambda) &= \langle\mathbf{p}\mu|v_{\kappa\lambda}(\mathbf{r})|\mathbf{p}\nu\rangle \\ &= -\tfrac{1}{2}\langle\mu|v_{\kappa\lambda}(\mathbf{r})|\nabla^2\nu\rangle - \tfrac{1}{2}\langle\nu|v_{\kappa\lambda}(\mathbf{r})|\nabla^2\mu\rangle \\ &\quad + \tfrac{1}{2}\langle\mu|[\nabla^2 v_{\kappa\lambda}(\mathbf{r})]|\nu\rangle,\end{aligned} \tag{33}$$

where $v_{\kappa\lambda}(\mathbf{r})$ is the Coulomb potential due to the charge distribution $\chi^*_\kappa(\mathbf{r})\chi_\lambda(\mathbf{r})$. The last term on the rhs of Eq. (33) is the two-electron Darwin term and is usually quite small. Furthermore, in the full expression (28), the negative contribution of this term is partially compensated by the positive contribution of the third term on the rhs of Eq. (28) depending on $O(c^{-4})$. Therefore, neglecting the two-electron Darwin term of order $O(c^{-2})$ in the second term of Eq. (28) together with the third term of Eq. (28) should lead to a better approximation than omitting the third term on the rhs of Eq. (28) alone.

However, omitting the two-electron Darwin term in Eq. (33) does not save much computational effort, because a large number of the additional integrals still need to be evaluated. A real simplification results when using the RI for the remaining two terms on the rhs of Eq. (28).[30] For a given basis set $|\chi\rangle$, the identity operator $\hat{I}$ can be represented according to Eq. (34),

$$\hat{I} = |\chi\rangle\mathbf{S}^{-1}\langle\chi|. \tag{34}$$

By inserting Eq. (34) between the operators $v_{\kappa\lambda}(\mathbf{r})$ and ∇^2 in Eq. (33), one obtains Eq. (35),

$$\begin{aligned}\frac{1}{m}(\mathbf{p}\mu\cdot\mathbf{p}\nu|\kappa\lambda) &\approx \sum_{\tau,\rho}(\mu\tau|\kappa\lambda)(\mathbf{S}^{-1})_{\tau\rho}T_{\rho\nu} \\ &\quad + \sum_{\tau,\rho}T_{\mu\tau}(\mathbf{S}^{-1})_{\tau\rho}(\rho\nu|\kappa\lambda) \\ &= \sum_{\tau}(\mu\tau|\kappa\lambda)Y_{\tau\nu} + \sum_{\rho}Y_{\rho\mu}(\rho\nu|\kappa\lambda),\end{aligned} \tag{35}$$

where the definition of the kinetic energy operator $-\nabla^2/(2m)$ (m, electron mass) was used and a new matrix $\mathbf{Y}$ defined in Eq. (36) was introduced.

$$\mathbf{Y} = \mathbf{S}^{-1}\mathbf{T}. \tag{36}$$

By inserting Eq. (35) into the reduced form of Eq. (28), one obtains Eq. (37),

TABLE III. Comparison of ground state energies (in hartree units) of heliumlike atomic ions calculated with the use of the exact two-electron integrals in Eq. (28) [omitting the Drawin and $O(c^{-4})$ terms] with the energies calculated with the use of Eq. (39).

a[a]	NESC-SORA (with exact $2\bar{e}$ integrals)	NESC-SORA (with approximate $2\bar{e}$ integrals)	Error[b]
60	−3 749.055 251 615 197	−3 749.055 251 616 833	1.64×10^{-9}
80	−6 999.041 033 114 926	−6 999.041 033 115 066	0.14×10^{-9}
100	−11 758.751 133 100 899	−11 758.751 133 105 879	4.98×10^{-9}

[a]Nuclear charge.
[b]Error due to the use of approximate integrals.

$$(\tilde{\mu}\tilde{\nu}|\tilde{\kappa}\tilde{\lambda}) \approx (\mu\nu|\kappa\lambda) + \frac{1}{2mc^2}\sum_{\tau\rho}[U^*_{\tau\mu}(\tau\rho|\kappa\lambda)X_{\rho\nu} + X^*_{\tau\mu}(\tau\rho|\kappa\lambda)U_{\rho\nu}] + \frac{1}{2mc^2} \times \sum_{\tau\rho}[U^*_{\tau\kappa}(\mu\nu|\tau\rho)X_{\rho\lambda} + X^*_{\tau\kappa}(\mu\nu|\tau\rho)U_{\rho\lambda}], \quad (37)$$

where the matrix $\mathbf{X}$ is defined in Eq. (38),

$$\mathbf{X} = \tfrac{1}{2}\mathbf{S}^{-1}\mathbf{T}\mathbf{U} = \tfrac{1}{2}\mathbf{Y}\mathbf{U}. \quad (38)$$

Using Eq. (37) for the modified two-electron integrals, the Coulomb contribution to the Fock operator becomes

$$\tilde{J}_{\mu\nu} = J_{\mu\nu} + \tilde{J}^{(a)}_{\mu\nu} + \tilde{J}^{(b)}_{\mu\nu}, \quad (39a)$$

$$J_{\mu\nu} = \sum_{\kappa\lambda}(\mu\nu|\kappa\lambda)D_{\kappa\lambda}, \quad (39b)$$

$$\tilde{J}^{(a)}_{\mu\nu} = \frac{1}{2mc^2}\sum_{\kappa\lambda}(\mu\nu|\kappa\lambda)R_{\kappa\lambda}, \quad (39c)$$

$$\tilde{J}^{(b)}_{\mu\nu} = \frac{1}{2mc^2}\sum_{\kappa\lambda}(U^*_{\kappa\mu}X_{\lambda\nu} + X^*_{\kappa\mu}U_{\lambda\nu})J_{\kappa\lambda}, \quad (39d)$$

where the matrix $\mathbf{R}$ is given in Eq. (40),

$$\mathbf{R} = \mathbf{U}\mathbf{D}\mathbf{X}^\dagger + \mathbf{X}\mathbf{D}^\dagger\mathbf{U}^\dagger. \quad (40)$$

For the exchange contribution Eq. (27b) one has a similar expression, however with the difference that, due to the spin-free approximation, the time-reversal part vanishes.[25] Thus, the calculation of the two-electron part can be carried out at essentially the same price as for the nonrelativistic calculation. The most time consuming part of this calculation is the evaluation of the two-electron integrals $(\mu\nu|\kappa\lambda)$, which has to be done only once when using Eq. (39).

Because the RI was used in deriving Eq. (39), a question about the accuracy of this approximation in comparison with the use of the exact two-electron integrals in Eqs. (33) and (28) seems appropriate. In Table III, the results of the NESC-SORA calculations carried out with the use of the exact integrals in Eq. (28) [omitting however the $O(c^{-4})$ terms and Darwin terms] and the results of approximate calculations employing Eq. (39) are reported. The difference between the two sets of calculations is less than 5×10^{-9} hartree units, which means that the use of RI does not lead to any noticeable error. Therefore, the results of NESC-SORA calculations employing Eq. (39) are reported in the fourth column of Table II.

With the use of Eq. (39), the lowest-order relativistic correction to the nonrelativistic electron-electron interaction energy is taken into account. In this approximation, the two-electron Darwin terms as well as the two-electron terms of order $O(c^{-4})$ in Eq. (28) are discarded. Compared to the last column of Table II, which presents results of calculations carried out with the nonrelativistic two-electron operator $J_{\mu\nu}$ only, this is a substantial improvement. It has to be emphasized that this improvement comes at no additional cost compared to that of a nonrelativistic calculation. In passing, we note that the same technique that was used in Eq. (39) to evaluate the relativistic two-electron integrals of order $O(c^{-2})$ can be used for the evaluation of the $O(c^{-4})$ terms. However, in this case, one would need to include the Darwin terms as well, which would lead to a certain increase in the computation time.

V. CONCLUSIONS

The regular approximation to the normalized elimination of the small component[16] in the modified Dirac equation has been developed and presented in matrix form. A comparison with the previously obtained IORA expressions reveals that the matrix formulation of the IORA method (previously derived using the RI),[14,15] is in fact the exact matrix representation of this method. The IORA method, either in matrix form[14,15] or in operator form,[10] represents a low-order approximation to NESC, which when compared to another low-order approximation to NESC, the so-called NESC ($\mathbf{U}=\mathbf{I}$) method,[26] has the advantage of being a variationally stable method. Therefore, it represents a suitable starting point for the development of improved NESC-based theories. It should be mentioned that the widely used ZORA method[8,9] represents the UESC-ZORA.[16]

In the next (second) order, the regular approximation to NESC, NESC-SORA, leads to a considerable improvement relative to the IORA energies. In fact, the NESC-SORA results are closer to the exact Dirac energies, as documented for a series of hydrogenlike ions, than the energies from the fifth-order Douglas–Kroll approximation DK5,[22] which is much more computationally demanding than NESC-SORA. It also should be stressed that the implementation of the NESC-SORA method can be achieved with the use of only those molecular integrals, which are routinely available in any nonrelativistic quantum-chemical program.

The approach was extended to the many-electron case, where a considerable reduction of the computational complexity was achieved with the use of the one-electron approximation in the relativistic transformation operators.[31,32] Within this approximation,[31,32] it is the nuclear attraction potential only that is used in the relativistic transformations. The two-electron terms neglected would make a $O(c^{-4})$ contribution to the transformed Hamiltonian. Thus, omitting these terms does not lead to noticeable errors. This is confirmed by the calculated energies of heliumlike atomic ions

with $Z=2-100$. The NESC-SORA ground state energies are in very good agreement with the results of the exact DHF calculations.

Application of IORA (=NESC-ZORA) and NESC-SORA to larger many-electron systems is hindered by the number of the two-electron integrals that need to be evaluated.[16,26] In a straightforward implementation, the same number of the two-electron integrals as in the full DHF method has to be evaluated.[16,26] However, with the use of the RI technique,[30] a drastic reduction in the number of integrals to be calculated is achieved. Now only those two-electron integrals, which would be evaluated in a nonrelativistic calculation anyway are needed. Therefore, the computational price of the new approximation is essentially the same as in the nonrelativistic case. Again, no new types of integrals are needed. Although the RI was used in developing this approximation, its accuracy is remarkable. In the calculations of heliumlike ions, the total energy based on the approximate integrals deviates from the energy calculated with the exact integrals by less than 5×10^{-9} hartree units.

One advantage of the NESC-SORA method over quasirelativistic methods based on the Foldy–Wouthuysen transformation,[33] such as the Douglas–Kroll approach,[21–23] is that there is no so-called picture change.[4,34] The wavefunction in the NESC-SORA method is normalized on the relativistic metric and no renormalization to the nonrelativistic metric is needed.[16] This simplifies greatly the calculation of molecular properties, where the picture change effects bring in an unnecessary complication.[4,34] Thus, the methodology developed in the present paper shows great promise for molecular calculations which will be the subject of subsequent papers.

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