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REGULAR ARTICLE

On convergence of the normalized elimination of the small component (NESC) method

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Abstract The convergence behavior of the iterative solution of the normalized elimination of the small component (NESC) method is investigated. A simple and efficient computational protocol for obtaining the exact positive-energy eigenvalues of the relativistic Hamiltonian starting from the energies obtained within the regular approximation is suggested. The protocol is based on the analysis of the relationship between the eigenvalues of the quasi-relativistic Hamiltonian in the regular approximation and the positive-energy eigenvalues of the exact relativistic Hamiltonian which was derived in the course of this work.

The first principles inclusion of relativistic effects into quantum chemical calculations is achieved with the use of the Dirac [2] (or Dirac–Fock [3,4]) equation. The four-component relativistic wave function contains information about both positive- and negative-energy states of the system [5]. In chemical applications, one is usually concerned with the electronic (or positive-energy) states only. Therefore, the use of a two-component quasi-relativistic approach seems to be preferred [6–10].

The method of the normalized elimination of the small component (NESC) developed by Dyall [11] furnishes a first principles two-component approach fully equivalent to the exact four-component relativistic theory in a finite basis set. An exact two-component approach very similar to NESC has recently been developed in Ref. [12]. The NESC method can be viewed as the most basic exact quasi-relativistic theory from which approximate quasi-relativistic methods, such as the regular approximation (RA) [13–16] or the Douglas–Kroll (DK) [17–21] method, can be derived [11,21].

The regular approximation (RA) in the form of the zeroth order regular approximation (ZORA) [14,15] or the infinite-order regular approximation (IORA) [16] methods furnishes perhaps the simplest approximate quasi-relativistic theory capable of yielding accurate results for the valence and sub-valence electronic shells in compounds of heavy elements [14–16,22]. However, if one is concerned with the theoretical calculation of properties depending on the atomic core electrons [22–24], the accuracy of these simple methods may be insufficient. Therefore, it is desirable to develop a simple and effective computational protocol for obtaining the exact results starting from the solutions provided by the RA methods. In this letter, we shall pursue the development of such a protocol.

A full derivation of the NESC method can be found in Ref. [11]. Here we begin with the NESC equation in matrix form [8],

$$\left(\mathbf{TU}+\mathbf{U}^{\dagger}\mathbf{T}-\mathbf{U}^{\dagger}\left[\mathbf{T}-\mathbf{W}\right]\mathbf{U}+\mathbf{V}\right)\mathbf{A} = \left(\mathbf{S}+\frac{1}{2mc^2}\mathbf{U}^{\dagger}\mathbf{TU}\right)\mathbf{AE}, \quad (1)$$

where the matrix representation of the operator $\mathbf{U}$, which connects the large ($\mathbf{A}$) and the pseudo-large ($\mathbf{B}=\mathbf{UA}$, cf. Eq. 20 in Ref. [11]) components of the four-component

This article is dedicated to Wim Nieuwpoort on the occasion of his 75th birthday.

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relativistic wave function modified according to Ref. [11], is given in Eq. 2:

$$\mathbf{U} = \mathbf{T}^{-1}\left[\mathbf{S}\tilde{\mathbf{S}}^{-1}\tilde{\mathbf{L}} - \mathbf{V}\right]. \tag{2}$$

In Eqs.1 and 2, **S**, **V** and **T** are the usual overlap, potential energy and kinetic energy matrices, respectively, and **W** is the matrix of the operator $\hat{W} = (\sigma \cdot \mathbf{p})V(\sigma \cdot \mathbf{p})/4m^2c^2$, where σ is the vector of Pauli matrices [25] and **p** is the linear momentum operator. In Eq. 2, $\tilde{\mathbf{L}}$ is the matrix of the hermitian quasi-relativistic Hamiltonian operator in parentheses on the left-hand side (LHS) of Eq. 1 and $\tilde{\mathbf{S}}$ is the normalization or metric matrix in parentheses on the right-hand side (RHS) of Eq. 1.

The expression for the operator **U** as given in Eq. 2 is modified as compared with the original expression (cf. Eq. 21 in Ref. [11]) with the use of the following matrix identities,

$$\mathbf{A}^{-1} = \mathbf{A}^{\dagger}\tilde{\mathbf{S}}, \tag{3}$$

$$\tilde{\mathbf{S}}^{-1} = \mathbf{A}\mathbf{A}^{\dagger}, \tag{4}$$

$$\tilde{\mathbf{L}} = \tilde{\mathbf{S}}\mathbf{A}\mathbf{E}\mathbf{A}^{\dagger}\tilde{\mathbf{S}}, \tag{5}$$

which follow from Eq. 1 and the wave function normalization condition $\mathbf{A}^{\dagger}\tilde{\mathbf{S}}\mathbf{A} = \mathbf{I}$.

The solution of Eq.1 can be found by iteration, starting from a reasonable approximation for the operator **U**, substituting it into Eq. 1 and iterating Eqs. 1 and 2 until convergence. The RA to the operator **U** and NESC equation (1) is provided in Eqs. 6 and 7 [21].

$$\mathbf{U}^{\mathrm{IORA}} = \left(\mathbf{T} - \mathbf{W}\right)^{-1}\mathbf{T}, \tag{6}$$

$$\tilde{\mathbf{L}}^{\mathrm{ZORA}}\mathbf{A}^{\mathrm{IORA}} = \tilde{\mathbf{S}}^{\mathrm{IORA}}\mathbf{A}^{\mathrm{IORA}}\mathbf{E}^{\mathrm{IORA}}, \tag{7a}$$

$$\tilde{\mathbf{L}}^{\mathrm{ZORA}} = \mathbf{T}\left(\mathbf{T} - \mathbf{W}\right)^{-1}\mathbf{T} + \mathbf{V}, \tag{7b}$$

$$\tilde{\mathbf{S}}^{\mathrm{IORA}} = \mathbf{S} + \frac{1}{2mc^2}\mathbf{T}\left(\mathbf{T}-\mathbf{W}\right)^{-1}\mathbf{T}\left(\mathbf{T}-\mathbf{W}\right)^{-1}\mathbf{T}. \tag{7c}$$

Note that Eq. 7 is the exact representation of the IORA equation in matrix form [21].

The outlined iterative procedure converges quickly to the exact solution of the Dirac equation, if the basis set does not contain very tight basis functions. However, the convergence of the iterations is destroyed by adding more steep basis functions to the basis set. This is illustrated in Table 1, where the results of the NESC calculation of hydrogen-like uranium U^{91+} are presented. The calculations employ even-tempered basis sets (ETBS) of 22, 24, 26 and 28 Gaussian s-type primitive functions with the exponential parameters obtained as $\alpha_i = ab^{i-1}$ with $a = 0.1$ and $b = 2$ [11]. The convergence to the exact Dirac energy is quick and stable with the smallest basis set. However, adding more steep functions leads to erratic convergence where spurious roots below the exact energy appear in the intermediate iterations. With the largest basis set in Table 1, the iterations diverge after a few first steps. This convergence behavior has nothing to do with kinetic balance [26], which is built into the NESC method, but rather indicates numeric instabilities in the calculation, the origin of which we shall try to analyze below.

Let us look more closely at the energy spectrum of the IORA method and its relationship to the energy spectrum of the Dirac equation. The energy spectrum of IORA is closely related to the energy spectrum of the so-called scaled ZORA method. [27,28] Indeed, the IORA equation can be derived by taking a variation of the Rayleigh quotient

$$E = \frac{\left\langle\Phi\middle|\hat{h}^{\mathrm{ZORA}}\middle|\Phi\right\rangle}{\left\langle\Phi\middle|1 + (\sigma \cdot \mathbf{p})\frac{c^2}{(2mc^2 - V)^2}(\sigma \cdot \mathbf{p})\middle|\Phi\right\rangle}, \tag{8}$$

with respect to the trial function Φ. The substitution (without variation) of the ZORA wave function into this quotient leads to the scaled ZORA method [27,28]. As the ZORA wave function is not the optimal wave function for IORA, the scaled ZORA energy is an upper bound to the IORA energy.

The ZORA energy is related to the Dirac energy E^{D} by [27,28]

$$E^{\mathrm{ZORA}} = \frac{2mc^2E^{\mathrm{D}}}{2mc^2 + E^{\mathrm{D}}} \quad . \tag{9}$$

This is the numerator of the above Rayleigh quotient for the ZORA wave function. The denominator of the Rayleigh quotient for the ZORA wave function is given by [27,28]

$$\left\langle\Phi\middle|1 + (\sigma \cdot \mathbf{p})\frac{c^2}{(2mc^2 - V)^2}(\sigma \cdot \mathbf{p})\middle|\Phi\right\rangle = 1 + \left|\frac{-E^{\mathrm{D}}}{2mc^2 + E^{\mathrm{D}}}\right|$$

$$= \begin{cases} \frac{2mc^2}{2mc^2+E^{\mathrm{D}}} & -2mc^2 < E^{\mathrm{D}} < 0 \\ \frac{2mc^2+2E^{\mathrm{D}}}{2mc^2+E^{\mathrm{D}}} & E^{\mathrm{D}} < -2mc^2 \quad \text{and} \quad E^{\mathrm{D}} > 0 \end{cases} . \tag{10}$$

With these two expressions, the mapping of the Dirac spectrum to that of the scaled ZORA method can be deduced:

$$E = \begin{cases} E^{\mathrm{D}} & -2mc^2 < E^{\mathrm{D}} < 0 \\ \frac{mc^2E^{\mathrm{D}}}{mc^2+E^{\mathrm{D}}} & E^{\mathrm{D}} < -2mc^2 \text{ and } E^{\mathrm{D}} > 0 \end{cases} . \tag{11}$$

The positive-energy bound states are situated in the interval $(-mc^2, 0)$, with no states below $-mc^2$. The positive-energy continuum (unbound) states of the Dirac spectrum $(0, +\infty)$ are mapped onto the interval $(0, +mc^2)$. The negative-energy continuum states of the Dirac spectrum $(-\infty, -2mc^2)$ are mapped onto the interval $(+mc^2, +2mc^2)$. These mappings apply also to the IORA spectrum. Additional confirmation of these

Table 1 Convergence of NESC equations (1), (2) to the exact eigenvalue for the ground state of U^{91+}

Iteration	22[a]	24	26	28
0	− 4869.4289038529	− 4902.3085045862	− 4914.3220171750	− 4918.6645554478
1	− 4812.2484730700	− 4843.7045820596	− 4855.1912386023	− 4859.3423047554
⋮	⋮	⋮	⋮	⋮
3	− 4811.7982285358	− 4843.2409574099	− 21641.4132342939	− 4858.8719305077
4	− 4811.7981739069	− 6917.8394951228	− 21534.3829288148	− 28408.4302411858
⋮	⋮	⋮	⋮	⋮
⋮	⋮	⋮	⋮	⋮
8	− 4811.7981726703	− 4843.2408994448	− 22086.6907049314	− 37909.3668094757
9	− 4811.7981726703	− 4843.2408994448	− 7960.0728275879	− 41685.9182374787
⋮			⋮	⋮
19			− 4854.7226035508	− 39706.9502819505
20			− 4854.7226035508	− 39525.5571083773

Convergence criterion 10^{-10} hartree. Exact analytic Dirac $1s_{1/2}$ eigenvalue is −4861.1980231194 hartree. See text for computational details

[a] Size of the basis set

ranges comes from a consideration of the free-particle IORA equation, which has exponentially decaying (bound) states below $E = 0$ and above $E = +2mc^2$, and oscillatory (free) states between $E = 0$ and $E = +2mc^2$. The above analysis shows that in the presence of an external potential $V(\mathbf{r})$, the IORA spectrum has no states above $+2mc^2$.

In basis set calculations, the matrix of the populations of the large component $\mathbf{P}_{\mathrm{L,L}}$, defined as in Eq. 12, can be used for the purpose of assignment of specific roots of a quasi-relativistic equation to the positive- or negative-energy branch of the Dirac spectrum:

$$\mathbf{P}_{\mathrm{L,L}} = \mathbf{A}^{\dagger}\mathbf{S}\mathbf{A}. \tag{12}$$

Indeed, $\left(\mathbf{P}_{\mathrm{L,L}}\right)_{kk} > 1/2$ for the states belonging to the positive-energy branch and $\left(\mathbf{P}_{\mathrm{L,L}}\right)_{kk} < 1/2$ for the states belonging to the negative-energy branch [29]. This relation can be deduced from the exact expression for the ratio of the small and large components. Using Eq. 12 with $\mathbf{A} = \mathbf{A}^{\mathrm{IORA}}$ to define $\mathbf{P}_{\mathrm{IORA,IORA}}$, analysis of the matrix IORA eigenvectors shows that (a) all states in the intervals $(-mc^2, 0)$ and $(0, +mc^2)$ belong to the positive-energy branch of the Dirac spectrum with $\left(\mathbf{P}_{\mathrm{IORA,IORA}}\right)_{kk} > 1/2$; (b) all states in the interval $(+mc^2, +2mc^2)$ belong to the negative-energy branch with $\left(\mathbf{P}_{\mathrm{IORA,IORA}}\right)_{kk} < 1/2$; (c) the IORA eigenstates above the limit of $+2mc^2$ formally belong to the negative-energy branch of the Dirac spectrum and possess $\left(\mathbf{P}_{\mathrm{IORA,IORA}}\right)_{kk} << 1/2$. These observations are consistent with the analysis above, but leave the problem of the interpretation of the states above $+2mc^2$.

A plausible hypothesis is that these states are mere artifacts of using a basis set of localized functions for the representation of highly energetic unbound states of an electron. Circumstantial evidence of the artificial nature of the IORA states above $+2mc^2$ is found in the fact that with the use of the same basis sets, the scaled ZORA method produces energies above its theoretical upper limit of $+2mc^2$. It is very likely that these numerical artifacts arise from the use of a Gaussian basis set with a point nuclear model, where the Dirac and the IORA wave function both have singularities.

A relationship between the eigenvalues of the IORA and NESC methods can be derived with the help of Eqs. 1 and 2. Let us multiply Eq. 1 from the left with $\mathbf{A}^{\dagger}$, substitute Eq. 2 into Eq. 1 and make use of identity (4) and wave function normalization. Then Eq. 1 transforms to Eq. 13 for the positive-energy eigenvalues of the exact relativistic equation:

$$\begin{aligned}\mathbf{E} = {} & \mathbf{A}^{\dagger}\mathbf{S}\mathbf{A}\mathbf{A}^{\dagger}\tilde{\mathbf{L}}\mathbf{A} + \mathbf{A}^{\dagger}\tilde{\mathbf{L}}\mathbf{A}\mathbf{A}^{\dagger}\mathbf{S}\mathbf{A} - \mathbf{A}^{\dagger}\mathbf{V}\mathbf{A} \\ & -\mathbf{A}^{\dagger}\left(\tilde{\mathbf{L}}\mathbf{A}\mathbf{A}^{\dagger}\mathbf{S} - \mathbf{V}\right)\mathbf{T}^{-1}(\mathbf{T} - \mathbf{W})\mathbf{T}^{-1} \\ & \times\left(\mathbf{S}\mathbf{A}\mathbf{A}^{\dagger}\tilde{\mathbf{L}} - \mathbf{V}\right)\mathbf{A}.\end{aligned} \tag{13}$$

Equation 13 can be simplified further with the use of Eqs. 7b and 14.

$$\begin{aligned}&\left(\tilde{\mathbf{L}}^{\mathrm{ZORA}} - \mathbf{V}\right)^{-1} \\ &= \left(\tilde{\mathbf{S}}^{\mathrm{IORA}}\mathbf{A}^{\mathrm{IORA}}\left(E^{\mathrm{IORA}} - (\mathbf{A}^{\mathrm{IORA}})^{\dagger}\mathbf{V}\mathbf{A}^{\mathrm{IORA}}\right)\right. \\ &\qquad \left.(\mathbf{A}^{\mathrm{IORA}})^{\dagger}\tilde{\mathbf{S}}^{\mathrm{IORA}}\right)^{-1} \qquad (14a) \\ &= (\tilde{\mathbf{S}}^{\mathrm{IORA}})^{-1}\left((\mathbf{A}^{\mathrm{IORA}})^{\dagger}\right)^{-1}\left(\mathbf{E}^{\mathrm{IORA}} - \bar{\mathbf{V}}_{\mathrm{IORA,IORA}}\right)^{-1}\end{aligned}$$

Table 2 Convergence of NESC equations (1), (17) to the exact eigenvalue for the ground state of U^{91+} as function of the cutoff parameter

Iteration	0[a]	$2mc^2$	$4mc^2$	$8mc^2$	$16mc^2$
0	−4918.6645554478	−4918.6645554478	−4918.6645554478	−4918.6645554478	−4918.6645554478
1	−4859.4660359668	−4859.3496751597	−4859.3453321671	−4859.3430238785	−4859.3425683596
⋮	⋮	⋮	⋮	⋮	⋮
8	−4858.8718712716	−4858.8718710079	−4858.8718709925	−4858.8718709919	−13784.5498744207
9	−4858.8718710734	−4858.8718709984	−4858.8718709921	−4858.8718709919	−13200.8050274110
⋮	⋮	⋮	⋮		⋮
11	−4858.8718710010	−4858.8718709920	−4858.8718709919		−4858.8718709920
12	−4858.8718709953	−4858.8718709920	−4858.8718709919		−5739.9016519270
13	−4858.8718709933				−4858.8718709920
14	−4858.8718709924				−4858.8718709920
⋮	⋮				
16	−4858.8718709920				
17	−4858.8718709920				

Convergence criterion 10^{-10} hartree. Exact analytic Dirac $1s_{1/2}$ eigenvalue is −4861.1980231194 hartree. See text for computational details.

[a] Value of the cutoff factor

$$\left(\mathbf{A}^{\mathrm{IORA}}\right)^{-1}\left(\tilde{\mathbf{S}}^{\mathrm{IORA}}\right)^{-1} \tag{14b}$$

$$= \mathbf{A}^{\mathrm{IORA}}\left(\mathbf{E}^{\mathrm{IORA}} - \bar{\mathbf{V}}_{\mathrm{IORA,IORA}}\right)^{-1}\left(\mathbf{A}^{\mathrm{IORA}}\right)^{\dagger} \tag{14c}$$

In Eq. 14, $\mathbf{A}^{\mathrm{IORA}}$ is the matrix of the expansion coefficients of the IORA eigenfunctions, $\mathbf{E}^{\mathrm{IORA}}$ is the diagonal matrix of the eigenvalues of the IORA equation (7a) and $\bar{\mathbf{V}}_{\mathrm{IORA,IORA}} = \left(\mathbf{A}^{\mathrm{IORA}}\right)^{\dagger}\mathbf{V}\mathbf{A}^{\mathrm{IORA}}$. When transforming Eq. 14b to Eq. 14c, the matrix identity (3) and its transposed counterpart were used.

With the use of Eqs. 7b and 14c, Eq. 13 is transformed to Eq. 15:

$$\begin{aligned}\mathbf{E} = {} & \mathbf{P}_{\mathrm{L,L}}\mathbf{E} + \mathbf{E}\mathbf{P}_{\mathrm{L,L}} - \bar{\mathbf{V}}_{\mathrm{L,L}} \\ & -\left(\mathbf{E}\left(\mathbf{P}_{\mathrm{IORA,L}}\right)^{\dagger} - \left(\bar{\mathbf{V}}_{\mathrm{IORA,L}}\right)^{\dagger}\right) \\ & \times\left(\mathbf{E}^{\mathrm{IORA}} - \bar{\mathbf{V}}_{\mathrm{IORA,IORA}}\right)^{-1} \\ & \times\left(\mathbf{P}_{\mathrm{IORA,L}}\mathbf{E} - \bar{\mathbf{V}}_{\mathrm{IORA,L}}\right),\end{aligned} \tag{15}$$

where $\bar{\mathbf{V}}_{\mathrm{L,L}} = \mathbf{A}^{\dagger}\mathbf{V}\mathbf{A}$, $\bar{\mathbf{V}}_{\mathrm{IORA,L}} = \left(\mathbf{A}^{\mathrm{IORA}}\right)^{\dagger}\mathbf{V}\mathbf{A}$ and $\mathbf{P}_{\mathrm{L,L}}$, $\mathbf{P}_{\mathrm{IORA,L}}$ are defined in Eqs. 12 and 16:

$$\mathbf{P}_{\mathrm{IORA,L}} = \left(\mathbf{A}^{\mathrm{IORA}}\right)^{\dagger}\mathbf{S}\mathbf{A}. \tag{16}$$

In Eqs. 15 and 16, $\mathbf{P}_{\mathrm{IORA,L}}$ has the meaning of an overlap of the IORA wave function $\mathbf{A}^{\mathrm{IORA}}$ with the large-component wave function $\mathbf{A}$. The IORA eigenstates in the intervals $(-mc^2, 0)$ and $(0, +mc^2)$, obtained in actual basis set calculations, possess nearly unit overlap with the respective converged large-component states. The overlap, however, rapidly decreases for the higher energy IORA eigenstates and becomes very (although non-negligibly) small for the IORA eigenstates above the $+2mc^2$ limit. From Eq. 15, it is obvious that the last term on the RHS, which is a positive (semi)definite matrix, can make a large negative contribution into the NESC eigenvalues provided that the overlap with certain starting guess (i.e., IORA) eigenvectors is greater than it should be. Taking into consideration the weird nature of the IORA eigenstates with the energies above $+2mc^2$, it may be suggested that it is the overlap with these spurious states that makes the iterative solution of the NESC equation unstable and leads to the emergence of unphysical solutions in the intermediate iterations.

This analysis suggests that we may project out all the spurious eigenvectors in order to restore the convergence. A simple way of achieving this is to restrict the number of eigenvectors used in the construction of the matrix $\mathbf{U}$, Eq. 2, to only those vectors that possess energy below a certain cutoff value ϵ^{up}, which can be chosen equal to $+2mc^2$, for example. This can be done by rewriting Eq. 2 as in Eq. 17:

$$\mathbf{U} = \mathbf{T}^{-1}\left[\mathbf{S}\mathbf{A}\mathbf{d}\mathbf{A}^{\dagger}\tilde{\mathbf{L}} - \mathbf{V}\right], \tag{17}$$

where $\mathbf{d}$ is a diagonal matrix with non-zero elements only for the eigenvectors $\mathbf{A}_k$ with $E_k \leq \epsilon^{\mathrm{up}}$. The non-zero elements are equal to unity. If the matrix $\mathbf{d}$ was the unit matrix, Eq. 17 would be exactly equivalent to Eq. 2 (cf. Eq. 4).

With this modification, the iterative solution of the NESC equations (1), (17) converges smoothly and rapidly to the exact relativistic value within the given basis

Table 3 Convergence of NESC equations (1), (17) with fuzzy cutoff condition (18) to the exact eigenvalue for the ground state of U^{91+} as function of the cutoff parameter

Iteration	28[a]	32	50	70
0	−4918.6645554478	−4920.5658600101	−4921.0992786884	−4921.0993652344
1	−4859.3553948714	−4861.1727043555	−4861.6825333833	−4861.6824951172
⋮	⋮	⋮	⋮	⋮
3	−4858.8719674680	−4860.6884602508	−4861.1980599164	−4861.1979980469
4	−4858.8718743707	−4860.6883668110	−4861.1979664564	−4861.1979980469
⋮	⋮	⋮	⋮	
7	−4858.8718709935	−4860.6883634256	−4861.1979629993	
8	−4858.8718709921	−4860.6883634242	−4861.1979629993	
9	−4858.8718709919	−4860.6883634240		
10	−4858.8718709919	−4860.6883634240		

Convergence criterion 10^{-10} hartree. Cutoff parameter of $+2mc^2$ is used in Eq. 18. Exact analytic Dirac $1s_{1/2}$ eigenvalue is −4861.1980231194 hartree. See text for computational details.
[a] Basis sets employed: ETBS-28, UGBS, UGBS-50 and UGBS-70

set. This is illustrated in Table 2, where the results of calculations of hydrogen-like uranium with the ETBS-28 are shown. Different values of the cutoff parameter ϵ^{up} are employed ranging from zero to $+16mc^2$. The converged energy does not depend on the specific value of the cutoff parameter (within the prescribed convergence criterion), although the convergence rate does. The results in Table 2 imply that (1) only energies of the bound states are needed to obtain the converged results for the bound electronic states; (2) however, neglecting the unbound states results in a poor convergence rate; (3) the convergence of the iterative solution of the NESC equation can still be achieved even if the unbound states above the upper limit $+2mc^2$ are present.

The last observation suggests that the effect of the spurious roots is largely suppressed during the iterations. Therefore, these roots may be retained in the iterative solution of the NESC equation, but their contribution should be damped with a fuzzy cutoff condition, such as the one given in Eq 18:

$$\mathbf{d}_k = \begin{cases} 1 & E_k \leq 0 \\ \left(1 + \frac{E_k}{\epsilon^{\mathrm{up}}}\right)^{-1} & E_k > 0 \end{cases}. \tag{18}$$

The results of calculations of hydrogen-like uranium carried out with the use of Eqs. 1, 17 and 18 are presented in Table 3. The basis sets employed are the ETBS-28, the universal Gaussian basis set (UGBS) of 32 primitive s-type functions [30], the UGBS extended with 18 tight functions obtained in even-tempered fashion using the ratio of the most tight functions in the original basis set and the UGBS extended with 38 tight functions. The convergence with the fuzzy cutoff condition is prompt and stable. Interestingly, the rate of convergence improves with larger basis sets.

In conclusion, a simple and efficient computational protocol for obtaining the exact positive-energy eigenvalues of the relativistic Hamiltonian starting from the energies obtained within the regular approximation is suggested. The protocol is based on the analysis of the relationship between the eigenvalues of the IORA method and the positive-energy eigenvalues of the exact relativistic Hamiltonian which was derived in the course of this work. The devised computational protocol guarantees prompt and stable convergence to the exact relativistic energies in a basis set representation. The convergence is monotonic (from below) which suggests that the convergence rate can be further improved with a suitable convergence engine, such as the direct inversion of the iteration space (DIIS) method. [31,32].

The analysis of the nature of IORA eigenvalues suggests that caution should be exercised when using these eigenvalues in correlated post-Hartree-Fock (HF) calculations and in response calculations. It may be suggested that only the virtual eigenvalues in the window $[0, +2mc^2]$ should be used. Alternatively, the basis sets employed in the IORA calculations should not contain very steep basis functions. These restrictions, however, do not apply to NESC, the eigenvalues of which can be used in further calculations without any additional constraints. The computational protocol suggested in the present work should lead to the development of a quasi-relativistic quantum chemical scheme comparable in its computational simplicity and effectiveness with the non-relativistic methods of electronic structure calculations, e.g., by combining it with computationally effective algo-

rithms for the calculation of the two-electron part of the relativistic Hamiltonian [21,33,34].

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