INFINITE-ORDER REGULAR APPROXIMATION BY THE METRIC PERTURBATION

Andrzej J. SADLEJ

Department of Quantum Chemistry, Institute of Chemistry, Nicolaus Copernicus University, PL-87 100 Torun, Poland; e-mail: teoajs@chem.uni.torun.pl

It is my great pleasure and honor to dedicate this paper to Professor Josef Paldus to celebrate his 70th birthday. Dear Joe, while recollecting our encounters it just came to my mind that there may be one more reason that 70 is a lucky number for celebrations. First, it was 40 years ago, in September 1965, that for the first time we met each other on Kalatówki. Then, it was 30 years ago, also in September, that we met again, this time on the other side of the "iron curtain", in Strasbourg. By some unorthodox arithmetics, this makes once again the lucky and unique number of 70. I cherish memories of both these meetings and I am pleased and happy to contribute to this volume. Happy birthday!

The regular approximation methods for the reduction of the Dirac equation to a fully equivalent two-component form are considered in the framework of the perturbation theory. The usual Dirac hamiltonian is first transformed with the change of metric. Then, the change of metric is considered as a perturbation to the zeroth-order (ZORA) problem. General formulae for perturbation corrections to the ZORA wave function and energy are expressed solely in terms of the two-component solutions. The method presented in this paper gives the energy-independent scheme for the step-by-step generation of the infinite-order results which are equivalent to solutions of the Dirac equations. Several formal and computational aspects of the infinite-order regular approximation are discussed. It is concluded that, because of the use of well-behaved operators, the high-order regular approximation methods can be considered as competitive to high-order Douglas–Kroll approaches.

Keywords: Relativistic methods; Regular approximation; ZORA; FORA; IORA; NESC method; Metric perturbation theory; Quantum mechanics; Quantum chemistry.

The attempts to formulate relativistic quantum mechanics solely in terms of two completely separable two-component theories, one for the so-called positive eigenspectrum and one for its negative part[1], are more than half a century old[2]. For most of the relativistic chemistry problems one could then focus on the positive energy solutions and this would make a fully relativistic theory for electrons only[3]. Such a reduced exact two-component

relativistic theory would be of great advantage, both computationally and conceptually[4].

The renewal of interest in either accurate or exact two-component methods for relativistic quantum chemistry goes back to the middle of 1980s when Hess[5,6] proposed a very eficient way of handling the approximate two-component relativistic hamiltonian of Douglas and Kroll[7] (DK). This was the beginning of what is nowadays referred to as the DK(DKH) method with all its modifications and extensions[4,8]. These developments have recently culminated in the formulation of the exact two-component relativistic theory for electrons only[9–11]. In this context one should also give credit to the important paper by Heully et al.[12], who proposed a convenient operator method for the removal of the off-diagonal blocks of the Dirac hamiltonian[12]. This method has been used by Barysz et al.[13] to analyze the structure of the DK approximation, and later, to carry out complete block-diagonalization of the Dirac hamiltonian[9–11].

Another important paper by Chang et al.[14], which appeared about the same time as the first papers of Hess[5,6], went initially unnoticed. It was only in the beginning of 1990s that Baerends, Snijders and their collaborators[15–18] independently proposed the same approach to the elimination of the so-called small component in the Dirac bi-spinor. This method became known as the zeroth-order regular approximation (ZORA) and was followed by its extended (first-order) approximation (FORA)[18]. More recently Dyall and van Lenthe have proposed the infinite-order (IORA) extension of the regular approximation[19] which is closely related to the earlier method of the normalized elimination of the small component (NESC) developed by Dyall[20] and very recently picked up by Filatov and Cremer[21].

The NESC approach which is expected to give the solution of the Dirac equation in terms of the so-called large component only. In the form proposed by Dyall[20] and used by Filatov and Cremer[21] the solution is obtained in energy-dependent form. Alternative approach, which leads to energy-independent matrix transformations, can be formulated in terms of the metric perturbation expansion[22,23]. This form of the infinite-order two-component method for electrons only, which is based on the idea of the elimination of the small component[20], will be discussed in the present paper.

THE ZORA EQUATION AS THE ZEROTH-ORDER OF THE METRIC PERTURBATION APPROACH

To define the objective of our considerations we shall summarize some of the basic ideas and equations of what is called the metric perturbation approach[22,23] and the related developments by Dyall[19,20]. Most of symbols used in this paper are either the same as those used by Dyall or closely follow his notation[19,20]. At variance with the methods pursued by Dyall[19,20] the present goal is to consider explicit perturbation approach to the indirect determination of the Dirac bi-spinor.

Let us consider the electron moving in external Coulomb field of the potential $V(\mathbf{r})$. The stationary Dirac equation (in atomic units) is

$$\mathbf{H}_0 \boldsymbol{\Psi} = E \boldsymbol{\Psi} \, , \tag{1}$$

where the bi-spinor $\boldsymbol{\Psi}$ is written in terms of the upper $\boldsymbol{\Psi}_L$ and lower $\boldsymbol{\Psi}_S$ two-component vectors

$$\boldsymbol{\Psi} = \begin{pmatrix} \boldsymbol{\Psi}_L \\ \boldsymbol{\Psi}_S \end{pmatrix} \tag{2}$$

and $\mathbf{H}_0$ is the usual Dirac hamiltonian[1,4]:

$$\mathbf{H}_0 = c\boldsymbol{\alpha p} + \beta c^2 + (V - c^2)I = \begin{pmatrix} V\mathbf{1} & c\boldsymbol{\sigma p} \\ c\boldsymbol{\sigma p} & (V - 2c^2)\mathbf{1} \end{pmatrix} \tag{3}$$

with I (**1**) denoting the 4×4 (2×2) unit matrix and $\boldsymbol{\alpha p}$ and β corresponding to Dirac matrices[1]. The bi-spinor $\boldsymbol{\Psi}$ is assumed to be normalized

$$\langle \boldsymbol{\Psi} | \boldsymbol{\Psi} \rangle = \langle \boldsymbol{\Psi}_L | \boldsymbol{\Psi}_L \rangle + \langle \boldsymbol{\Psi}_S | \boldsymbol{\Psi}_S \rangle = 1 \tag{4}$$

with the norm of the upper (large) component assumed to be larger than that of the lower (small) component. Upon transforming the initial bi-spinor according to

$$\boldsymbol{\Psi} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \frac{1}{2}\alpha\boldsymbol{\sigma p} \end{pmatrix} \begin{pmatrix} \boldsymbol{\Psi}_L \\ \boldsymbol{\Phi}_L \end{pmatrix} = \mathbf{S}^{1/2}\boldsymbol{\Phi} \, , \tag{5}$$

where $\alpha = 1/c$, the Dirac equation becomes

$$\mathbf{H}_1\boldsymbol{\Phi} = E\mathbf{S}\boldsymbol{\Phi} \tag{6}$$

with the new hamiltonian defined by

$$\mathbf{H}_1 = \mathbf{S}^{1/2}\mathbf{H}_0\mathbf{S}^{1/2} = \begin{pmatrix} V\mathbf{1} & T\mathbf{1} \\ T\mathbf{1} & \frac{1}{4}\alpha^2\,\boldsymbol{\sigma}\boldsymbol{p}V\boldsymbol{\sigma}\boldsymbol{p} - T\mathbf{1} \end{pmatrix}, \tag{7}$$

where $T = 1/2\,\boldsymbol{\sigma}\boldsymbol{p}\boldsymbol{\sigma}\boldsymbol{p} = 1/2p^2$ is the nonrelativistic kinetic energy operator. The norm of $\boldsymbol{\Phi}$ with respect to the new metric $\mathbf{S}$, follows from

$$\langle\boldsymbol{\Psi}|\boldsymbol{\Psi}\rangle = \langle\boldsymbol{\Phi}|\mathbf{S}|\boldsymbol{\Phi}\rangle = \langle\boldsymbol{\Psi}_\mathrm{L}|\boldsymbol{\Psi}_\mathrm{L}\rangle + \langle\boldsymbol{\Phi}_\mathrm{L}|\tfrac{1}{4}\alpha^2\boldsymbol{\sigma}\boldsymbol{p}\boldsymbol{\sigma}\boldsymbol{p}|\boldsymbol{\Phi}_\mathrm{L}\rangle = 1 \ . \tag{8}$$

This way of transforming the original Dirac equation by introducing the pseudolarge component $\boldsymbol{\Phi}_\mathrm{L}$ is analogous to the transformation introduced by Rutkowski[24–26] in what is known as the direct perturbation theory (DPT)[27,28]. Hence, a similar approach can be used in the present case by applying the perturbation theory ideas to the matrix $\mathbf{S}$. For this reason let us consider the following perturbation partition of $\mathbf{S}$:

$$\mathbf{S} = \mathbf{S}(\lambda) = \mathbf{S}^{(0)} + \lambda\mathbf{S}^{(1)} \ , \tag{9}$$

where

$$\mathbf{S}^{(0)} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}, \qquad \mathbf{S}^{(1)} = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \frac{1}{4}\alpha^2\,\boldsymbol{\sigma}\boldsymbol{p}\boldsymbol{\sigma}\boldsymbol{p} \end{pmatrix} \tag{10}$$

and λ is a formal perturbation parameter which orders the perturbation series and is set equal to either 0 or 1 whenever appropriate. The first-order term with respect to λ will be considered as the perturbation to the zeroth-order problem

$$\mathbf{H}^{(0)}\boldsymbol{\Phi}^{(0)} = E^{(0)}\mathbf{S}^{(0)}\boldsymbol{\Phi}^{(0)} \ , \tag{11}$$

where $\mathbf{H}^{(0)} = \mathbf{H}_1$ of Eq. (*7*) and

$$\boldsymbol{\Phi}^{(0)} = \begin{pmatrix} \boldsymbol{\Psi}_\mathrm{L}^{(0)} \\ \boldsymbol{\Phi}_\mathrm{L}^{(0)} \end{pmatrix}. \tag{12}$$

By writing Eq. (*11*) in the form of a set of 2×2 matrix equations[20]:

$$V\boldsymbol{\Psi}_\mathrm{L}^{(0)} + T\boldsymbol{\Phi}_\mathrm{L}^{(0)} = E^{(0)}\boldsymbol{\Psi}_\mathrm{L}^{(0)}$$

$$T\boldsymbol{\Psi}_\mathrm{L}^{(0)} + \left(\frac{1}{4}\alpha^2\,\boldsymbol{\sigma}\boldsymbol{p}V\boldsymbol{\sigma}\boldsymbol{p} - T\right)\boldsymbol{\Phi}_\mathrm{L}^{(0)} = 0 \tag{13}$$

one finds that the pseudolarge component $\boldsymbol{\Phi}_\mathrm{L}^{(0)}$ of $\boldsymbol{\Phi}^{(0)}$ can be determined as

$$\Phi_{\mathrm{L}}^{(0)} = \frac{1}{p^2}\alpha^2\,\boldsymbol{\sigma p}B\boldsymbol{\sigma p}\Psi_{\mathrm{L}}^{(0)}\,,\tag{14}$$

where $B = (1 - 1/2\alpha^2 V)^{-1}$. Its substitution into the first matrix equation in (*13*) gives the familiar ZORA equation for $\Psi_{\mathrm{L}}^{(0)}$ (refs[15,17,22,23]):

$$\left(\frac{1}{2}\boldsymbol{\sigma p}B\boldsymbol{\sigma p} + V\right)\Psi_{\mathrm{L}}^{(0)} = E^{(0)}\Psi_{\mathrm{L}}^{(0)}\,.\tag{15}$$

Moreover, according to Eq. (*8*) the normalization condition for $\Phi^{(0)}$, i.e., through the zeroth-order in λ, reads:

$$\langle\Phi^{(0)}|\boldsymbol{S}^{(0)}|\Psi^{(0)}\rangle = \langle\Phi_{\mathrm{L}}^{(0)}|\Psi_{\mathrm{L}}^{(0)}\rangle = 1\,.\tag{16}$$

To summarize this survey of basic equations[19,20,22,23] let us note that from the point of view of the transformation (*5*) the ZORA approach can be considered as a method which actually follows from the elimination of the small component. In the zeroth-order (with respect to λ) approximation $\Psi^{(0)}$ to the Dirac solution Ψ the corresponding zeroth-order approximation for its small component reads:

$$\Psi_{\mathrm{S}}^{(0)} = \frac{1}{2}\alpha\boldsymbol{\sigma p}\Phi_{\mathrm{L}}^{(0)}\,.\tag{17}$$

Hence, once the ZORA two-component wave function $\Phi^{(0)}$ is determined, one can easily obtain the zeroth-order approximation to the Dirac bispinor. As shown in the next section, the metric perturbation approach can be used to generate the Dirac solution of arbitrarily high accuracy.

INFINITE-ORDER SOLUTION BY THE METRIC PERTURBATION METHOD

Let us start with Eq. (*6*) which can be reorganized to the manifestly perturbative form:

$$\mathbf{H}^{(0)}\Phi = E(\mathbf{S}^{(0)} + \lambda\mathbf{S}^{(1)})\Phi\,.\tag{18}$$

This suggests that both Φ and E can be expanded into power series in λ.

$$\Phi = \Phi(\lambda) = \Phi^{(0)} + \lambda\Phi^{(1)} + \lambda^2\Phi^{(2)} + \dots\tag{19}$$

$$E = E(\lambda) = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots\tag{20}$$

The same holds also for the large (Ψ_L) and pseudolarge (Φ_L) components of Φ.

$$\Psi_L = \Psi_L(\lambda) = \Psi_L^{(0)} + \lambda\Psi_L^{(1)} + \lambda^2\Psi_L^{(2)} + \ldots \tag{21}$$

$$\Phi_L = \Phi_L(\lambda) = \Phi_L^{(0)} + \lambda\Phi_L^{(1)} + \lambda^2\Phi_L^{(2)} + \ldots \tag{22}$$

The zeroth-order terms in Eqs (*19*)–(*22*) are the solutions of the ZORA equation. In the *n*-th order ($n \geq 1$) one obtains the following set of inhomogeneous equations:

$$(V - E^{(0)})\Psi_L^{(n)} + T\Phi_L^{(n)} = E^{(n)}\Psi_L^{(n)} + \sum_{r=1}^{n} E^{(r)}\Psi_L^{(n-r)} \tag{23}$$

$$T\Psi_L^{(n)} + \left(\frac{1}{4}\alpha^2\,\boldsymbol{\sigma p}V\boldsymbol{\sigma p} - T\right)\Phi_L^{(n)} = \frac{1}{2}\alpha^2 \sum_{r=0}^{n-1} E^{(r)}\,p^2\,\Phi_L^{(n-r-1)} \ . \tag{24}$$

One should note that the r.h.s. of these equations is fully determined by solutions of the order lower than n and can be assumed to be available. Hence, the *n*-th order pseudolarge component $\Phi_L^{(n)}$ can be determined from Eq. (*24*) in terms of some known functions and the *n*-th order large component $\Psi_L^{(n)}$:

$$\Phi_L^{(n)} = \frac{1}{p^2}\,\boldsymbol{\sigma p}B\boldsymbol{\sigma p}\Psi_L^{(n)} - \frac{1}{2}\alpha^2 \sum_{r=0}^{n-1} E^{(r)}\,\frac{1}{p^2}\,\boldsymbol{\sigma p}B\boldsymbol{\sigma p}\Phi_L^{(n-r-1)} \ , \tag{25}$$

which in turn can be substituted into Eq. (*23*), leading to:

$$(\mathbf{h}^{(0)} - E^{(0)})\Psi_L^{(n)} = \sum_{r=1}^{n} E^{(r)}\Psi_L^{(n-r)} + \frac{1}{4}\alpha^2 \sum_{r=0}^{n-1} E^{(r)}\boldsymbol{\sigma p}B\boldsymbol{\sigma p}\Phi_L^{(n-r-1)} \ , \tag{26}$$

where

$$\mathbf{h}^{(0)} = \frac{1}{2}\boldsymbol{\sigma p}B\boldsymbol{\sigma p} + V \tag{27}$$

is the two-component ZORA hamiltonian.

It appears to be instructive to write down the explicit form of Eq. (*26*) for a few lowest values of *n*. For $n = 1$ we obtain:

$$(\mathbf{h}^{(0)} - E^{(0)})\Psi_L^{(1)} = E^{(1)}\Psi_L^{(0)} + \frac{1}{4}\alpha^2 E^{(0)}\boldsymbol{\sigma p}B^2\,\boldsymbol{\sigma p}\Psi_L^{(0)} \ . \tag{28}$$

The first-order energy correction $E^{(1)}$ can be obtained by projecting this equation onto $\langle\Psi_L^{(0)}|$. With the use of the zeroth-order normalization condition (*16*) this correction becomes

$$E^{(1)} = -\frac{1}{4}\alpha^2 E^{(0)}\langle\Psi_L^{(0)}/\boldsymbol{\sigma p}B^2\boldsymbol{\sigma p}/\Psi_L^{(0)}\rangle\,. \tag{29}$$

The second-order perturbed equation in its explicit form is given by:

$$(\mathbf{h}^{(0)} - E^{(0)})\Psi_L^{(2)} = E^{(1)}\Psi_L^{(1)} + E^{(2)}\Psi_L^{(0)} + \frac{1}{4}\alpha^2 E^{(0)}\boldsymbol{\sigma p}B^2\boldsymbol{\sigma p}\Psi_L^{(1)} +$$

$$+ \frac{1}{4}\alpha^2 E^{(1)}\boldsymbol{\sigma p}B^2\boldsymbol{\sigma p}\Psi_L^{(0)} - \frac{1}{8}\alpha^4 E^{(0)}E^{(0)}\boldsymbol{\sigma p}B^3\boldsymbol{\sigma p}\Psi_L^{(0)} \tag{30}$$

with the second-order energy correction $E^{(2)}$ evaluated as:

$$E^{(2)} = \frac{1}{8}\alpha^4 E^{(0)}E^{(0)}\langle\Psi_L^{(0)}/\boldsymbol{\sigma p}B^3\boldsymbol{\sigma p}/\Psi_L^{(0)}\rangle -$$

$$- \frac{1}{4}\alpha^2 E^{(1)}\langle\Psi_L^{(0)}/\boldsymbol{\sigma p}B^2\boldsymbol{\sigma p}/\Psi_L^{(0)}\rangle -$$

$$- \frac{1}{4}\alpha^2 E^{(0)}\langle\Psi_L^{(0)}/\boldsymbol{\sigma p}B^2\boldsymbol{\sigma p}/\Psi_L^{(1)}\rangle - E^{(1)}\langle\Psi_L^{(0)}/\Psi_L^{(1)}\rangle\,. \tag{31}$$

One should note that the second-order energy correction involves the renormalization contribution $E^{(1)}\langle\Psi_L^{(0)}|\Psi_L^{(1)}\rangle$. This means that $\Psi_L^{(1)}$ must satisfy the first-order normalization condition:

$$\langle\Psi_L^{(0)}|\Psi_L^{(1)}\rangle + \langle\Psi_L^{(1)}|\Psi_L^{(0)}\rangle + \frac{1}{4}\alpha^2\langle\Phi_L^{(0)}/\boldsymbol{\sigma p}\boldsymbol{\sigma p}/\Phi_L^{(0)}\rangle = 0 \tag{32}$$

which follows from the expansion of (*8*). This condition can be easily satisfied by supplementing $\Psi_L^{(1)}$ with a term proportional to $\Psi_L^{(0)}$, i.e., with the solution of the homogeneous counterpart of (*28*). The higher-order energy corrections will obviously involve higher-order renormalization terms which can be dealt with in the same way.

Another possibility to cope with the renormalization problem is to assume the the so-called intermediate normalization condition for $\langle\Psi_L|$:

$$\langle\Psi_L^{(0)}|\Psi_L\rangle = 1\,. \tag{33}$$

This condition will greatly simplify the handling of Eq. (*26*). However, to recover the Dirac bi-spinor from solutions satisfying the intermediate normalization (*33*) the a posteriori renormalization will have to be performed. This will be particularly important in calculations of expectation values of different property-related operators.

The process of generating perturbation corrections to the ZORA solution $\Psi_L^{(0)}$ can be continued to higher orders in λ. In the n-th order one obtains then a partial sum:

$$E(n) = E^{(0)} + E^{(1)} + \ldots + E^{(n)} , \tag{34}$$

which approximates the Dirac energy through terms of the order of α^{2N}. Because of the dependence of the B operator on α^2, the partial sum (*34*) will also contain some part of contributions from all higher orders in α^2. Thus, adding $E^{(1)}$ to the ZORA energy $E^{(0)}$ gives the approximate total energy which is exact through the order of α^2 (refs[13,22,23]). This is actually the FORA energy[15,16,22,23]. In a similar way the partial sum $E(2)$ will give an approximation to the Dirac energy which is exact through terms of the order of α^4 and contaminated by some contributions of the higher order in α^2. The $E(2)$ expression is equivalent to the second-order regular approximation (SORA)[13].

One should also mention that the approach presented in this paper is closely related to the DPT method of Rutkowski and Kutzelnigg[24–28]. In the present case, however, the only perturbation term arises from the change of metric. In DPT the zeroth-order approximation corresponds to the two-component Schrödinger equation known as the Levy–Leblond equation[27,28]. Thus, the DPT expansion starts from the nonrelativistic zeroth-order level. In the case of the metric perturbation method, the zeroth-order level, i.e., the ZORA approximation, includes some terms of infinite order in α^2. This can be considered as an advantage of the ZORA approach and the metric perturbation method built upon it. On the other hand, there is a certain disadvantage, since the ZORA and all finite-order RA approximations depend on the gauge of the Coulomb potential[18].

In the sense of its strategy, the present metric perturbation approach is to some extent similar to the development of the n-order methods (DKn) based on the DK approximation[8]. Starting from some initial approximation one tries to improve upon it by completing the theory through a certain order in α^2. In the case of the DK approach, the numerical solution of the infinite-order is feasible[4,10,11] and leads to the complete separation of the electronic and positronic spectra.

In two-component methods based on the DK scheme, the major profit comes comes from the initial unitary transformation of the Dirac hamiltonian by the free particle Foldy–Wouthuysen matrix[4,7,13]. However, this transformation involves some not-too-well defined operators, e.g., square roots of expressions involving the p^2 operators, which may lead to ill-behaved energy dependence on α^2 (refs[3,29,30]). Although these operators can be efficiently dealt with by using the approximate identity resolution into states which diagonalize the p^2 operator, the problem remains and is likely to be responsible for the odd behavior of the n-th order DK approximations for certain values of n (e.g., for n = 4, 5)[8,11,31,32].

The metric perturbation method profits from the initial change of metric (*5*) which, in the sense of the metric perturbation method, gives the ZORA method as the zeroth-order approximation. First, by virtue of the transformation (*5*), the zeroth-order approximation automatically satisfies what is called the kinetic balance condition[20]. Second, the operator *B*, which appears in the ZORA hamiltonian and then enters all perturbation corrections, is manifestly nonsingular and well-behaved[18]. Hence, some of the formal problems of the DK(*n*) methods can be avoided in the metric perturbation approach[3].

There are also some negative aspects of the initial zeroth-order approximation used in the metric perturbation approach. It is known[18] that the ZORA approximation suffers from the gauge noninvariance of the electrostatic potential. This gauge dependence is, however, strongly diminished already in the FORA method and will be further reduced on introducing the higher-order corrections.

Finally, it is worthwhile to stress that the metric perturbation method is fully expressed in terms of two-component functions. Once some sufficiently (numerically) accurate approximation to Ψ_L is obtained, the bispinor solution can be generated by the inverse transformation and used to calculate other than energy properties of the given system. Such a method would be free of what is known as the change of picture of the corresponding property-related operators[33–36]. Equivalently, one can express the operator expectation values explicitly in terms of Ψ_L. Then, however, the operator must undergo the appropriate transformation[34]. Which of the two routes to obtain the expectation values is easier depends on its computational implementation. Nevertheless, claiming that methods, which express the Dirac solution solely in terms of its large component, are free of the change of picture problem is not quite correct[21].

COMMENTS AND CONCLUSIONS

Following the ideas of the metric perturbation approach[22,23] with the ZORA equation as the zeroth-order approximation, a compact form of the corresponding theory has been presented and discussed. Though at the first sight the basic equation to be solved, i.e., Eq. (*26*), may look forbidding, its solution can be generated iteratively by using some selected set of (two-component) basis functions[18–20,37]. The easiest way is to use the reduced resolvent operator defined in terms of two-component states which diagonalize the ZORA operator (*27*). This technique is commonly used in many-body perturbation methods[38] and can be conveniently employed to obtain matrix approximations to the solution of Eq. (*26*). The algebraic approach to the order-by-order solution of Eq. (*26*) can be continued until the desired accuracy is achieved. In this sense the theory presented in this paper can be regarded as the infinite-order method which generates the Dirac solution of the desired accuracy. This is exactly the same meaning of infinity as used in the case of the IORA [19] and the infinite-order DK methods[10,11].

At variance with the IORA and NESC methods considered by Dyall[19,20] the metric perturbation approach does not depend on the total energy. The r.h.s. of Eq. (*26*) solely depends on the data available from the lower-order solutions. This is the advantage of using the perturbation approach rather than the energy-dependent iterative method. Moreover, the present formalism permits step-by-step study of different finite-order regular approximations. The ordering of the perturbation series follows from Eq. (*9*).

The theory developed in this study was presented for one-electron solutions. Its extension to many-electron problems can be accomplished in the same way as in the case of other ZORA-based methods[18–20,37]. The most likely implementation of the present scheme will be in the framework of the Dirac–Coulomb approximation.

On comparing the DK and ZORA-type methods one finds several similarities, though there are significant differences as well. Both these approaches can be made into infinite-order methods for the generation of Dirac bi-spinors. In both cases one tries to express these bi-spinors solely in terms of the large component. Although the earlier IORA and NESC methods and the present perturbation approach do not attempt to explicitly block-diagonalize to Dirac hamiltonian, all of them try to reduce the computational task to two-component formalism. The infinite-order DK approach leads to the complete block-diagonalization of the Dirac hamiltonian and the corresponding two-component solution is obtained without explicit reference to the small component part of the Dirac bi-spinor. Once the iter-

ative solutions in the infinite-order DK method and in the present metric perturbation approach are well enough converged, there is no difference between the two; both of them will generate the Dirac solutions. However, there may be some important difference between finite-order DK and metric perturbation methods. From this point of view the approach based on finite (low) order approximations to the metric perturbation approach may offer certain advantages because of the well-behaved character of the B operator. As exemplified by the success of the low-order RA methods[18,19] the finite-order metric perturbation schemes can be considered as competitive to higher-order DK approximations.

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