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REGULAR ARTICLE

Comparison of restricted, unrestricted, inverse, and dual kinetic balances for four-component relativistic calculations

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Abstract Various kinetic balances for constructing appropriate basis sets in four-component relativistic calculations are examined in great detail. These include the well-known restricted (RKB) and unrestricted (UKB) kinetic balances, the less-known dual kinetic balance (DKB) as well as the unknown inverse kinetic balance (IKB). The RKB and IKB are complementary to each other: The former is good for positive-energy states, whereas the latter good for negative-energy states. The DKB combines the good of both RKB and IKB and even provides full variational safety. However, such an advantage is largely offset by its complicated nature. The UKB does not offer any particular advantages as well. Overall, the RKB is the simplest ansatz. Although the negative-energy states by a finite RKB basis are in error of $O(c^0)$, there is no objection to using them as intermediates for a sum-over-states formulation of perturbation theory, provided that the magnetic balance is also incorporated in the case of magnetic properties. In particular, the RKB is also an essential ingredient for formulating two-component relativistic theories, while all the others are simply incompatible. As such, the RKB should be regarded as the cornerstone of relativistic electronic structure calculations.

Keywords Restricted kinetic balance · Unrestricted kinetic balance · Inverse kinetic balance · Dual kinetic balance · Magnetic balance

Dedicated to Professor Pekka Pyykkö on the occasion of his 70th birthday and published as part of the Pyykkö Festschrift Issue.

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1 Introduction

Early attempts [1] to solve the Dirac equation in a basis expansion were plagued by the occurrence of matrix eigenvalues in the *forbidden region* between the lowest positive-energy and the highest negative-energy operator eigenvalues. This phenomenon has usually been called (in a slightly misleading way) *variational collapse* and was often traced back to the lack of a lower-bound property of the Dirac operator. Actually, the 'variational collapse' is due to the fact that inappropriately chosen basis sets are unable to describe the kinetic energy correctly and to guarantee the correct non-relativistic limit (nrl) [2, 3]. It can be removed *without* the need to impose a lower-bound property on the matrix representation of the Dirac equation.

Among the various strategies [4–7] to avoid the variational collapse, the restricted kinetic balance (RKB) [8–10]

has turned out to be particularly useful. To make this plausible in the spirit of 'elimination of the small component', we start from the Dirac equation in block form

$$h_D\psi_i = W_i\psi_i, \tag{1}$$

$$h_D = \begin{pmatrix} mc^2 + V & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & -mc^2 + V \end{pmatrix}, \quad \psi_i = \begin{pmatrix} \psi_i^L \\ \psi_i^S \end{pmatrix} \tag{2}$$

for a single electron subject to the nuclear attraction V, which has eigenstates with both $W_i > 0$ and $W_i < 0$. The negative-energy states (NES) can be removed by imposing the *key relation* (KR) between the upper and lower components of the positive-energy states (PES) [11–14]

$$\psi_i^S = X\psi_i^L, \tag{3}$$

where X is the solution of the implicit equation

$$2mc^2X = c\vec{\sigma}\cdot\vec{p} - [X, V] - cX\vec{\sigma}\cdot\vec{p}X. \tag{4}$$

If one knew X, one could eliminate the lower components ψ_i^S from the Dirac Eq. 1 and arrive at a theory in terms of the upper components ψ_i^L, viz., an exact two-component theory for electrons only with an operator h_+ that is bounded from below and allows a variational treatment. Unfortunately, Eq. 4 cannot be solved, except for a free particle. However, one may replace the exact X by its nrl

$$cX = cX_0 + O(c^{-2}), \quad cX_0 = \frac{1}{2m}\vec{\sigma}\cdot\vec{p} \tag{5}$$

in order to be correct at least in the nrl, viz.,

$$(T+V)\psi_i^{L(0)} = \epsilon_i^{(0)}\psi_i^{L(0)}, \quad T = \frac{p^2}{2m},$$
$$\epsilon_i^{(0)} = W_i^{(0)} - mc^2, \quad \psi_i^{S(0)} = \frac{1}{2mc}\vec{\sigma}\cdot\vec{p}\psi_i^{L(0)}. \tag{6}$$

Strictly speaking, the above nrl is only valid for a non-singular potential V [15]. However, such a subtlety is immaterial for the present purpose. One gains flexibility if one does not impose relation (5) directly between ψ_i^L and ψ_i^S but between the individual basis functions

$$\psi_i^L = \sum_{\mu=1}^{2N^L} g_\mu \mathbf{A}_{\mu i}; \quad \psi_i^S = \sum_{\mu=1}^{2N^L} f_\mu \mathbf{B}_{\mu i}; \quad f_\mu = \frac{1}{2mc}\vec{\sigma}\cdot\vec{p}g_\mu \tag{7}$$

with coefficients **A** and **B** independent. This is just the RKB prescription.

As for the NES, one must impose the *inverse key relation* (IKR):

$$\psi_i^L = -X^\dagger\psi_i^S \tag{8}$$

with the same X as before. The nrl is then

$$(-T+V)\psi_i^{S(0)} = \epsilon_i^{(0)}\psi_i^{S(0)}, \quad \epsilon_i^{(0)} = W_i^{(0)} + mc^2,$$
$$\psi_i^{L(0)} = -\frac{1}{2mc}\vec{\sigma}\cdot\vec{p}\psi_i^{S(0)}, \tag{9}$$

which would suggest immediately an 'inverse kinetic balance' (IKB)

$$\psi_i^L = \sum_{\mu=1}^{2N^L} f_\mu \mathbf{A}_{\mu i}^I; \quad \psi_i^S = \sum_{\mu=1}^{2N^L} g_\mu \mathbf{B}_{\mu i}^I; \quad f_\mu = \frac{1}{2mc}\vec{\sigma}\cdot\vec{p}g_\mu. \tag{10}$$

From the just-given 'derivation' of the RKB and IKB, one is easily led to two *incorrect* conclusions, which are still quite popular in the literature: (a) PES can only be expanded in a RKB basis, whereas NES only in an IKB basis; (b) The energies of PES are in error of $O(c^{-4})$ even with a complete RKB basis such that only the leading relativistic correction is taken care of.

In reality, as we shall show, both PES and NES can be expanded *exactly* in either a RKB or an IKB basis. Only the convergence with respect to the basis size is slower if PES are described with the IKB or NES with the RKB. It has been shown [16] that, for an even-tempered RKB Gaussian basis, the error ε^R of the energy for the ground state of a hydrogenic ion depends on the dimension N of the basis as

$$\varepsilon^R \sim \exp(-\pi\sqrt{[3+\gamma]N}), \quad \gamma = \sqrt{1 - \frac{Z^2}{c^2}} - 1 \approx -\frac{Z^2}{2c^2}. \tag{11}$$

Compared with the non-relativistic counterpart [17]

$$\varepsilon^{NR} \sim \exp(-\pi\sqrt{3N}), \tag{12}$$

the relativistic error ε^R is somewhat larger and converges more slowly with the basis size, but not so in a spectacular way. The wave function converges in a L^2 norm and the rate of convergence is essentially the same for the upper and lower components in spite of the singularities.

To understand better the role of the RKB, we note that a *variational collapse* is even possible in non-relativistic theory. Let us start from the non-relativistic energy expectation value

$$E = \frac{\langle\psi|V|\psi\rangle + \frac{1}{2}\langle\nabla\psi|\nabla\psi\rangle}{\langle\psi|\psi\rangle}. \tag{13}$$

Assume now that the basis $\{\phi_k\}$ is complete for the expansion of ψ, but that the functions $\{\nabla\phi_k\}$ are not defined, or that $\nabla\psi$ is not expandable in $\{\nabla\phi_k\}$. Then, we will fail to get the eigenvalues of the Hamiltonian by extrapolation from those of its matrix representation. It is an old wisdom in mathematical physics, ignored in quantum chemistry until 1977 [18], that for convergence to the exact eigenstates in the mean, it is necessary and sufficient that the basis $\{\phi_k\}$ is complete in the *first Sobolev space*, implying that $\nabla\psi$ is expandable in $\{\nabla\phi_k\}$. The natural relativistic generalization of completeness in the first Sobolev space is to require that $\{\vec{\sigma}\cdot\vec{p}g_\mu\}$ is defined for an otherwise complete basis $\{g_\mu\}$. This is achieved for a RKB basis. There is strong evidence for this but a rigorous mathematical proof is still lacking.

At first glance, the KR (3) and the RKB (7) look rather similar, and the motivation for introducing the latter has actually been to find a simplified form of the former. This is why the KR has often *erroneously* been referred to as *exact balance* and the RKB accordingly as *approximate balance*. There are two fundamental differences between the two concepts:

1. The KR is an explicit relation between the *upper and lower components* ψ_i^L and ψ_i^S of the bispinor ψ_i, while the RKB is a relation between the *basis functions* g_μ and f_μ into which ψ_i^L and ψ_i^S are expanded. The latter is a direct relation between ψ_i^L and ψ_i^S *only in the nrl*. If both ψ_i^L and ψ_i^S are interpreted as generally contracted functions, the last equality in (6) just says that the small-component basis functions $\{f_\mu\}$ should directly be generated by the action of $\vec{\sigma}\cdot\vec{p}$ on the large-component ones $\{g_\mu\}$ and that the same contraction coefficients can be chosen for the small and large components only in the nrl. The former is just Eq. 7.
2. The introduction of the KR is to formulate two-component theories for electrons only, a highly non-trivial issue [19], while that of the RKB is to properly represent the Dirac equation in a finite basis. That is, the RKB does *not* eliminate negative-energy states but remains a theory in terms of four-component spinors.

Nonetheless, the RKB and the matrix counterpart [20] of the KR can be combined to formulate two-component relativistic theories in a simple way, actually in one step [20–32]. In other words, the RKB is also an essential ingredient, viz., a built-in condition, for two-component relativistic theories, a point fully recognized only recently [32]. This applies to all existing two-component theories, whether approximate or exact.

We postpone closer comparisons between the RKB and IKB to Sect. 2, where the unrestricted kinetic balance (UKB) [10, 33] and the dual kinetic balance (DKB) [34] are also discussed. Section 3 is devoted to numerical assessments of the four kinetic balances, where nuclear magnetic resonance (NMR) shielding constants are also taken as a probe to reveal the quality of the NES. The account ends with concluding remarks and perspectives in Sect. 4.

2 Matrix representation of the Dirac equation

From now on, the rest-mass energy mc^2 is to be subtracted from the Dirac Eq. 1 to align the energy scale with the non-relativistic one. The zero point energy of NES is then reset to $-2mc^2$ rather than the previous $-mc^2$. Plain and boldface letters are used to denote operators and matrices, respectively. When necessary, the NES are denoted by barred indices. The Einstein summation convention over repeated indices is always employed.

2.1 RKB

The RKB prescription (7) leads to the following matrix Dirac equation

$$\begin{pmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & \frac{1}{4m^2c^2}\mathbf{W}-\mathbf{T} \end{pmatrix}\begin{pmatrix} \mathbf{A} \\ \mathbf{B} \end{pmatrix} = \begin{pmatrix} \mathbf{S} & 0 \\ 0 & \frac{1}{2mc^2}\mathbf{T} \end{pmatrix}\begin{pmatrix} \mathbf{A} \\ \mathbf{B} \end{pmatrix}\epsilon, \quad (14)$$

in which the individual matrices are all of dimension $2N^L$ with the elements defined as

$$\begin{aligned} \mathbf{V}_{\mu\nu} &= \langle g_\mu|V|g_\nu\rangle, \quad \mathbf{T}_{\mu\nu} = \langle g_\mu|T|g_\nu\rangle \\ &= \frac{1}{2m}\langle\vec{\sigma}\cdot\vec{p}g_\mu|\vec{\sigma}\cdot\vec{p}g_\nu\rangle, \quad \mathbf{S}_{\mu\nu} = \langle g_\mu|g_\nu\rangle, \\ \mathbf{W}_{\mu\nu} &= \langle\vec{\sigma}\cdot\vec{p}g_\mu|V|\vec{\sigma}\cdot\vec{p}g_\nu\rangle = \langle g_\mu|\vec{\sigma}\cdot\vec{p}V\vec{\sigma}\cdot\vec{p}|g_\nu\rangle. \end{aligned} \quad (15)$$

Equation 14 is therefore of dimension $4N^L$ with $2N^L$ PES and $2N^L$ NES. This is equivalent to making the following transformation of the original Dirac equation:

$$h_D^M\psi_i^M = S^M\psi_i^M\epsilon_i, \quad (16)$$

$$\mathcal{T}_M = \begin{pmatrix} 1 & 0 \\ 0 & \frac{\vec{\sigma}\cdot\vec{p}}{2mc} \end{pmatrix}, \quad (17)$$

$$h_D^M = \mathcal{T}_M^\dagger h_D \mathcal{T}_M = \begin{pmatrix} V & T \\ T & \frac{1}{4m^2c^2}\vec{\sigma}\cdot\vec{p}V\vec{\sigma}\cdot\vec{p}-T \end{pmatrix}, \quad (18)$$

$$S^M = \mathcal{T}_M^\dagger\mathcal{T}_M = \begin{pmatrix} 1 & 0 \\ 0 & \frac{1}{2mc^2}T \end{pmatrix}, \quad (19)$$

$$\psi_i^M = \mathcal{T}_M^{-1}\psi_i = \begin{pmatrix} \psi_i^L \\ \phi_i^L \end{pmatrix}, \quad \psi_i^S = \frac{\vec{\sigma}\cdot\vec{p}}{2mc}\phi_i^L \quad (20)$$

Obviously, the large ($\psi_i{}^L$) and pseudo-large ($\phi_i{}^L$) components have the same symmetry properties. This "modified Dirac equation" (16) was first proposed by Kutzelnigg [4] and then explored more thoroughly by Dyall [35]. It was pointed out [32] recently that the large and pseudo-large components must be expanded in the same basis $\{g_\mu\}$ in order to guarantee the correct nrl, a prerequisite to ensure that the energies of the PES are correct to $O(c^{-2})$. The matrix representation of Eq. 16 is then just Eq. 14, that of the original Dirac equation in a RKB basis. That is, there is no 'modified matrix Dirac equation', often called in the literature though.

The nrl of Eq. 16 for the PES is the same as Eq. 6 but with $\phi_i^{L(0)} = \psi_i^{L(0)}$, whereas for the NES, it is

$$\begin{aligned} (-2mT^2 + \vec{\sigma}\cdot\vec{p}V\vec{\sigma}\cdot\vec{p})\phi_{\bar{i}}^{L(0)} &= 2mT\phi_{\bar{i}}^{L(0)}\epsilon_{\bar{i}}^{(0)}, \\ \psi_{\bar{i}}^{L(0)} &= -\frac{1}{2mc^2}T\phi_{\bar{i}}^{L(0)}. \end{aligned} \quad (21)$$

In accordance with this, the nrl of Eq. 14 for the PES and NES are respectively

$$(\mathbf{T}+\mathbf{V})\mathbf{A}^{(0)}=\mathbf{S}\mathbf{A}^{(0)}\epsilon^{(0)},\quad \mathbf{B}^{(0)}=\mathbf{A}^{(0)}, \tag{22}$$

$$\begin{aligned}&(-2m\mathbf{T}\mathbf{S}^{-1}\mathbf{T}+\mathbf{W})\mathbf{B}^{(0)}=2m\mathbf{T}\mathbf{B}^{(0)}\bar{\epsilon}^{(0)},\\ &\mathbf{A}^{(0)}=-\frac{1}{2mc^2}\mathbf{S}^{-1}\mathbf{T}\mathbf{B}^{(0)}.\end{aligned} \tag{23}$$

It is seen that the correct nrl (22) for the PES is guaranteed even with a finite RKB basis. This stems directly from the fact [36] that such a finite basis already provides an *exact* matrix representation of the operator identity $(\vec{\sigma}\cdot\vec{p})(\vec{\sigma}\cdot\vec{p})=\vec{p}^2 I_2$. However, Eq. 23 is only an approximation to the matrix representation of Eq. 9 in the $\{\vec{\sigma}\cdot\vec{p}g_\mu\}$ basis or to that of Eq. 21 in the $\{g_\mu\}$ basis, viz.,

$$(-2m\mathcal{T}+\mathbf{W})\mathbf{B}^{(0)}=2m\mathbf{T}\mathbf{B}^{(0)}\bar{\epsilon}^{(0)},\quad \mathcal{T}_{\mu\nu}=\langle g_\mu|T^2|g_\nu\rangle. \tag{24}$$

As the matrix $\mathbf{T}\mathbf{S}^{-1}\mathbf{T}$ is positive definite, Eq. 23 always underestimates the kinetic energy (in absolute scale), unless the basis set is complete. That is, the energies of the NES by a finite RKB basis are in error of $O(c^0)$. One might then argue that such NES are of little value for the evaluation of response properties through the sum-over-states (sos) formulation of perturbation theory. However, such an argument should be viewed with caution. Mathematically, the NES are just part of the basis for properly discretizing property operators, and their errors of $O(c^0)$ are just like those of the PES arising from the incompleteness in the large-component basis. It will be shown later on that this is indeed the case.

2.2 IKB

The IKB prescription (10) gives rise to the following matrix representation of the Dirac equation

$$\begin{pmatrix}\frac{1}{4mc^2}\mathbf{W} & \mathbf{T}\\ \mathbf{T} & \mathbf{V}-2mc^2\mathbf{S}\end{pmatrix}\begin{pmatrix}\mathbf{A}^I\\ \mathbf{B}^I\end{pmatrix}=\begin{pmatrix}\frac{1}{2mc^2}\mathbf{T} & 0\\ 0 & \mathbf{S}\end{pmatrix}\begin{pmatrix}\mathbf{A}^I\\ \mathbf{B}^I\end{pmatrix}\epsilon^I, \tag{25}$$

which could have been obtained by the replacements of $\mathbf{V}\rightarrow-\mathbf{V}$, $\mathbf{W}\rightarrow-\mathbf{W}$, $\epsilon\rightarrow-\epsilon^I-2mc^2\mathbf{I}$, $\mathbf{A}\rightarrow-\mathbf{B}^I$, and $\mathbf{B}\rightarrow\mathbf{A}^I$ in Eq. 14, as requited by charge conjugation symmetry for the interchange of particles and antiparticles. That is, the PES and NES of the RKB with potential V (or $-V$) are just mirror images of the respective NES and PES of the IKB with potential $-V$ (or V), provided that the upper- and lower-component basis functions are also interchanged. It is interesting to note that, the transformation $(\mathbf{A},\mathbf{B})^T\rightarrow(-\mathbf{B}^I,\mathbf{A}^I)^T$ proceeds through Kramers pairs (ψ_i and $\mathcal{K}\psi_i$) because of the simple relation between the charge conjugation ($\mathcal{C}$) and time reversal ($\mathcal{K}$) operators, i.e, $\mathcal{C}=-\beta\gamma_5\mathcal{K}$. The IKB is equivalent to making a transformation $\mathcal{T}_I$ to the original Dirac equation:

$$h_D^I\psi_i^I=S^I\psi_i^I\epsilon_i, \tag{26}$$

$$h_D^I=\mathcal{T}_I^\dagger h_D\mathcal{T}_I=\begin{pmatrix}\frac{1}{4m^2c^2}\vec{\sigma}\cdot\vec{p}V\vec{\sigma}\cdot\vec{p} & T\\ T & V-2mc^2\end{pmatrix}, \tag{27}$$

$$\mathcal{T}_I=\begin{pmatrix}\frac{\vec{\sigma}\cdot\vec{p}}{2mc} & 0\\ 0 & 1\end{pmatrix}, \tag{28}$$

$$S^I=\mathcal{T}_I^\dagger\mathcal{T}_I=\begin{pmatrix}\frac{1}{2mc^2}T & 0\\ 0 & 1\end{pmatrix}, \tag{29}$$

$$\psi_i^I=\mathcal{T}_I^{-1}\psi_i=\begin{pmatrix}\phi_i^S\\ \psi_i^S\end{pmatrix},\quad \psi_i^L=\frac{\vec{\sigma}\cdot\vec{p}}{2mc}\phi_i^S. \tag{30}$$

The small ($\psi^S{}_i$) and pseudo-small ($\phi^S{}_i$) components have the same symmetry properties and should hence be expanded in the same basis $\{g_\mu\}$. In the nrl, we have $\psi_i^{S(0)}=\frac{1}{2mc^2}T\phi_i^{S(0)}$ for the PES and $\phi_i^{S(0)}=-\psi_i^{S(0)}$ for the NES. In accordance with this, the nrl of (25) for the PES and NES are respectively

$$\begin{aligned}&(2m\mathbf{T}\mathbf{S}^{-1}\mathbf{T}+\mathbf{W})\mathbf{A}^{I(0)}=2m\mathbf{T}\mathbf{A}^{I(0)}\epsilon^{I(0)},\\ &\mathbf{B}^{I(0)}=\frac{1}{2mc^2}\mathbf{S}^{-1}\mathbf{T}\mathbf{A}^{I(0)},\end{aligned} \tag{31}$$

$$(-\mathbf{T}+\mathbf{V})\mathbf{B}^{I(0)}=\mathbf{S}\mathbf{B}^{I(0)}\bar{\epsilon}^{(0)},\quad \mathbf{A}^{I(0)}=-\mathbf{B}^{I(0)}. \tag{32}$$

It is seen that Eqs. 31 and 32 are the matrix representations of Eqs. 6 and 9 in the $\{\vec{\sigma}\cdot\vec{p}g_\mu\}$ and $\{g_\mu\}$ bases, respectively. Now, it is the former that is an approximation to the matrix Schrödinger equation

$$(2m\mathcal{T}+\mathbf{W})\mathbf{A}^{I(0)}=2m\mathbf{T}\mathbf{A}^{I(0)}\epsilon^{(0)},\quad \mathcal{T}_{\mu\nu}=\langle g_\mu|T^2|g_\nu\rangle. \tag{33}$$

In other words, the nrl for the PES cannot be obtained correctly with a finite IKB basis as the kinetic energy is always underestimated.

There is a logic difference between the use of a RKB and an IKB basis. If one wants to describe s or p states in a RKB basis, one can just use s or p functions. In contrast, if one wants to construct the same states in an IKB basis, one ought to use $p_{1/2}$ functions for s states, a combined $s_{1/2}$-$d_{3/2}$ basis for $p_{1/2}$ states, and $d_{3/2}$ functions for $p_{3/2}$ states.

2.3 DKB

If one realizes that the RKB is the method of choice for PES, while the IKB is appropriate for NES, one may attempt to combine the two basis sets such that the combined basis is good for both types of states. However, this is not recommended since the basis is overcomplete and suffers from numerical instability problems. Instead, one can invoke the so-called dual kinetic balance (DKB) [34], viz.,

$$\psi_i^L = \sum_{\mu=1}^{2N^L} \begin{pmatrix} g_\mu \\ \frac{1}{2mc}\vec{\sigma}\cdot\vec{p}g_\mu \end{pmatrix} \mathbf{A}^D_{\mu i}, \qquad \psi_i^S = \sum_{\mu=1}^{2N^L} \begin{pmatrix} -\frac{1}{2mc}\vec{\sigma}\cdot\vec{p}f_\mu \\ f_\mu \end{pmatrix} \mathbf{B}^D_{\mu i}, \tag{34}$$

$$g_\mu = R^L_\mu(r)\Omega_{\kappa,m_j}(\hat{r}), \quad \kappa = (-1)^{j+l+1/2}(j+1/2), \tag{35}$$

$$f_\mu = iR^S_\mu(r)\Omega_{-\kappa,m_j}(\hat{r}). \tag{36}$$

Note that a pair of g_μ and f_μ functions is of opposite parity. The negative sign before $\vec{\sigma}\cdot\vec{p}$ in the second equality of (34) stems from the last equality in Eq. 9 and is in line with charge conjugation symmetry. Without such a sign, the two subspaces of (34) will be 'entangled', viz. of non-vanishing off-diagonal elements in the metric. This may result in 'inverse variational collapse', i.e., some NES might occur above $-2mc^2$. On the other hand, the imaginary unity in (36) is only necessary to make the radial Dirac equation real-valued (see "Appendix"). The corresponding matrix representation of the Dirac equation reads

$$\begin{aligned} &\begin{pmatrix} \mathbf{T}^{LL}+\mathbf{V}^{LL}+\frac{1}{4m^2c^2}\mathbf{W}^{LL} & \frac{1}{2mc}\mathbf{W}^{LS} \\ \frac{1}{2mc}\mathbf{W}^{SL} & \mathbf{V}^{SS}-2\mathbf{T}^{SS}+\frac{1}{4m^2c^2}\mathbf{W}^{SS}-2mc^2\mathbf{S}^{SS} \end{pmatrix} \\ &\times \begin{pmatrix} \mathbf{A}^D \\ \mathbf{B}^D \end{pmatrix} \\ &= \begin{pmatrix} \mathbf{S}^{LL}+\frac{1}{2mc^2}\mathbf{T}^{LL} & 0 \\ 0 & \mathbf{S}^{SS}+\frac{1}{2mc^2}\mathbf{T}^{SS} \end{pmatrix} \begin{pmatrix} \mathbf{A}^D \\ \mathbf{B}^D \end{pmatrix} \epsilon^D, \end{aligned} \tag{37}$$

where

$$\begin{aligned} \mathbf{T}^{LL}_{\mu\nu} &= \langle g_\mu|T|g_\nu\rangle, \quad \mathbf{V}^{LL}_{\mu\nu} = \langle g_\mu|V|g_\nu\rangle, \\ \mathbf{W}^{LL}_{\mu\nu} &= \langle g_\mu|\vec{\sigma}\cdot\vec{p}V\vec{\sigma}\cdot\vec{p}|g_\nu\rangle, \quad \mathbf{S}^{LL}_{\mu\nu} = \langle g_\mu|g_\nu\rangle, \\ \mathbf{W}^{LS}_{\mu\nu} &= \langle g_\mu|\vec{\sigma}\cdot\vec{p}V - V\vec{\sigma}\cdot\vec{p} - T\vec{\sigma}\cdot\vec{p}|f_\nu\rangle, \\ \mathbf{W}^{SL}_{\mu\nu} &= \langle f_\mu|V\vec{\sigma}\cdot\vec{p} - \vec{\sigma}\cdot\vec{p}V - \vec{\sigma}\cdot\vec{p}T|g_\nu\rangle, \\ \mathbf{T}^{SS}_{\mu\nu} &= \langle f_\mu|T|f_\nu\rangle, \quad \mathbf{V}^{SS}_{\mu\nu} = \langle f_\mu|V|f_\nu\rangle, \\ \mathbf{W}^{SS}_{\mu\nu} &= \langle f_\mu|\vec{\sigma}\cdot\vec{p}V\vec{\sigma}\cdot\vec{p}|f_\nu\rangle, \quad \mathbf{S}^{SS}_{\mu\nu} = \langle f_\mu|f_\nu\rangle. \end{aligned} \tag{38}$$

This is equivalent to making a $\mathcal{T}_D$ transformation of the original Dirac equation:

$$h_D^D\psi_i^D = S^D\psi_i^D\epsilon_i, \tag{39}$$

$$\mathcal{T}_D = \begin{pmatrix} 1 & -\frac{\vec{\sigma}\cdot\vec{p}}{2mc} \\ \frac{\vec{\sigma}\cdot\vec{p}}{2mc} & 1 \end{pmatrix}, \tag{40}$$

$$\begin{aligned} h_D^D &= \mathcal{T}_D^\dagger h_D \mathcal{T}_D, \\ &= \begin{pmatrix} V+T+\frac{1}{4m^2c^2}\vec{\sigma}\cdot\vec{p}V\vec{\sigma}\cdot\vec{p} & \frac{1}{2mc}(\vec{\sigma}\cdot\vec{p}V - V\vec{\sigma}\cdot\vec{p} - T\vec{\sigma}\cdot\vec{p}) \\ \frac{1}{2mc}(V\vec{\sigma}\cdot\vec{p} - \vec{\sigma}\cdot\vec{p}V - \vec{\sigma}\cdot\vec{p}T) & V-2T+\frac{1}{4m^2c^2}\vec{\sigma}\cdot\vec{p}V\vec{\sigma}\cdot\vec{p}-2mc^2 \end{pmatrix}, \end{aligned} \tag{41}$$

$$S^D = \mathcal{T}_D^\dagger\mathcal{T}_D = \begin{pmatrix} 1+\frac{1}{2mc^2}T & 0 \\ 0 & 1+\frac{1}{2mc^2}T \end{pmatrix}, \tag{42}$$

$$\begin{aligned} \psi_i^D &= \mathcal{T}_D^{-1}\psi_i = \begin{pmatrix} \tilde{\psi}_i^L \\ \tilde{\psi}_i^S \end{pmatrix}, \text{ or } \begin{pmatrix} \psi_i^L \\ \psi_i^S \end{pmatrix} \\ &= \begin{pmatrix} \tilde{\psi}_i^L - \frac{1}{2mc}\vec{\sigma}\cdot\vec{p}\tilde{\psi}_i^S \\ \tilde{\psi}_i^S + \frac{1}{2mc}\vec{\sigma}\cdot\vec{p}\tilde{\psi}_i^L \end{pmatrix}. \end{aligned} \tag{43}$$

Just like the original large (ψ_i^L) and small (ψ_i^S) components, the so-modified large ($\tilde{\psi}_i^L$) and small ($\tilde{\psi}_i^S$) components are of opposite parity and should hence be expanded in terms of the $\{g_\mu\}$ and $\{f_\mu\}$ functions of opposite parity, respectively. The nrl of Eq. 39 for the respective PES and NES are Eq. 6 with $\tilde{\psi}_i^{L(0)} = \psi_i^{L(0)}$ and $\tilde{\psi}_i^S = 0$ and Eq. 9 with $\tilde{\psi}_i^{S(0)} = \psi_i^{S(0)}$ and $\tilde{\psi}_i^L = 0$. In line with these, the nrl of Eq. 37 for the PES and NES are respectively

$$(\mathbf{T}^{LL}+\mathbf{V}^{LL})\mathbf{A}^{D(0)} = \mathbf{S}^{LL}\mathbf{A}^{D(0)}\epsilon^{(0)}, \quad \mathbf{B}^{D(0)} = 0, \tag{44}$$

$$(-\mathbf{T}^{SS}+\mathbf{V}^{SS})\mathbf{B}^{D(0)} = \mathbf{S}^{SS}\mathbf{B}^{D(0)}\bar{\epsilon}^{(0)}, \quad \mathbf{A}^{D(0)} = 0, \tag{45}$$

which are both correct even with a finite DKB basis.

The transformation $\mathcal{T}_D$ (40) may further, in the spirit of the Foldy–Wouthuysen unitary transformation [37], be generalized to

$$U_p = e^\tau, \quad \tau = -\frac{1}{2mc}\beta\vec{\alpha}\cdot\vec{p} = -\tau^\dagger, \quad U_pU_p^\dagger = 1, \tag{46}$$

which gives rise to the following modified Dirac equation

$$\tilde{h}\tilde{\psi}_i = \tilde{\psi}_i\epsilon_i, \tag{47}$$

$$\tilde{h} = U_p^\dagger h_D U_p, \quad \tilde{\psi}_i = U^\dagger\psi_i. \tag{48}$$

It is seen that $\mathcal{T}_D = 1+\tau$ is just a linearized form of the whole U_p. It can also be viewed as the nrl of the decoupling part of the FW unitary transformation if the latter is split into two parts, a decoupling and a renormalization [13]. However, this does not mean that Eq. 39 is an approximation to Eq. 47 because the former involves a non-unit matrix S^D. The problem with Eq. 47 lies in that the transformed Hamiltonian $\tilde{h}$ does not terminate in the Baker–Campbell–Hausdorff expansion and furthermore involves complicated integrals. This option will therefore not be considered any more.

2.4 UKB

Another widely used prescription for constructing a four-component basis is the UKB, although it offers no particular advantages over the RKB from both formal and practical aspects [32]. To make the present account more complete, we decide to present this prescription in detail. At variance with the RKB which invokes the fixed

combinations of $(\sigma_x p_x + \sigma_y p_y + \sigma_z p_z) g_\mu$, the UKB amounts to lifting this "restriction" so as to offer more flexibility for describing the small component. That is, an UKB basis for the small component is no longer one-to-one correspondent with that for the large component but $\{\vec{\sigma}\cdot\vec{p}g_\mu, \mu = 1,\ldots,2N^L\}$ must be a subset of the whole small-component basis $\{f_\mu, \mu = 1,\ldots,2N^S; N^S > N^L\}$ to guarantee the correct nrl. The expansion

$$\psi_i^L = \sum_{\mu=1}^{2N^L} g_\mu \mathbf{A}_{\mu i}^U, \quad \psi_i^S = \sum_{\mu=1}^{2N^S} f_\mu \mathbf{B}_{\mu i}^U \tag{49}$$

gives rise to the following matrix representation of the Dirac equation:

$$\begin{pmatrix} \mathbf{V}^{LL} & c\Pi^{LS} \\ c\Pi^{SL} & \mathbf{V}^{SS} - 2c^2\mathbf{S}^{SS} \end{pmatrix} \begin{pmatrix} \mathbf{A}^U \\ \mathbf{B}^U \end{pmatrix} = \begin{pmatrix} \mathbf{S}^{LL} & 0 \\ 0 & \mathbf{S}^{SS} \end{pmatrix} \begin{pmatrix} \mathbf{A}^U \\ \mathbf{B}^U \end{pmatrix} \mathbf{E}, \tag{50}$$

where

$$\mathbf{V}_{\mu\nu}^{LL} = \langle g_\mu | V | g_\nu \rangle, \quad \mathbf{V}_{\mu\nu}^{SS} = \langle f_\mu | V | f_\nu \rangle, \quad \Pi_{\mu\nu}^{LS} = \langle g_\mu | \vec{\sigma}\cdot\vec{p} | f_\nu \rangle,$$
$$\Pi_{\mu\nu}^{SL} = \langle f_\mu | \vec{\sigma}\cdot\vec{p} | g_\nu \rangle, \quad \mathbf{S}_{\mu\nu}^{LL} = \langle g_\mu | g_\nu \rangle, \quad \mathbf{S}_{\mu\nu}^{SS} = \langle f_\mu | f_\nu \rangle. \tag{51}$$

The way of constructing an UKB basis is not unique. Here, we consider two choices, spinor- and scalar-UKB [38]. To make the description clear, we have to first examine the RKB prescription in some detail. Define a spherical Gaussian spinor g_μ for the large component as

$$g_\mu = N_{\mu l} r^{n-1} e^{-\zeta_\mu r^2} \Omega_{\kappa,m_j}(\vartheta,\varphi) = R_{\mu,\kappa}^L(r)\Omega_{\kappa,m_j}(\vartheta,\varphi), \quad n \geq 1. \tag{52}$$

Usually, only spherical functions of principal quantum number n equal to $l+1$ are adopted in the calculation. The action of $\vec{\sigma}\cdot\vec{p}$ on g_μ leads to

$$\vec{\sigma}\cdot\vec{p}g_\mu = -i\left[\frac{d}{dr} + \frac{\kappa+1}{r}\right] R_{\mu,\kappa}^L(r)\Omega_{-\kappa,m_j}(\vartheta,\varphi) \tag{53}$$

$$= -iR_{\mu,\kappa}^S(r)\Omega_{-\kappa,m_j}(\vartheta,\varphi), \tag{54}$$

$$R_{\mu,\kappa}^S(r) = \left[\frac{\kappa+n}{r} - 2\zeta_\mu r\right] R_{\mu,\kappa}^L(r). \tag{55}$$

That is, $\vec{\sigma}\cdot\vec{p}$ changes the sign of κ in the angular function and generates a combined radial function $R^S_{\mu,\kappa}(r)$ (55).

For the case of $\kappa < 0$, e.g., $1s_{1/2}$, $2p_{3/2}$, $3d_{5/2}$, etc., we have $n = l+1 = -\kappa$ for the large component and $l^S = l+1$ for the small component. Equation 55 then reduces to

$$R_{\mu,\kappa}^S(r) = -2\zeta_\mu f_{\mu,\kappa}^S(r), \quad f_{\mu,\kappa}^S(r) = r^{l^S} e^{-\zeta_\mu r^2}, \quad l^S = l+1 = -\kappa, \tag{56}$$

which is a function of $n^S = l^S + 1 = l + 2 = n + 1$. That is, a $1s_{1/2}$ function with exponent ζ_μ is to be kinetically balanced by a $2p_{1/2}$ function of the same exponent, $2p_{3/2}$ by $3d_{3/2}$, $3d_{5/2}$ by $4f_{5/2}$, and so on.

For the case of $\kappa > 0$, e.g., $2p_{1/2}$, $3d_{3/2}$, $4f_{5/2}$, etc., we have $n = l+1$ and $\kappa = l$ for the large component and $l^S = l-1$ for the small component. Equation 55 can therefore be written as

$$R_{\mu,\kappa}^S(r) = \left[(2l^S+3) - 2\zeta_\mu r^2\right] f_{\mu,\kappa}^S(r), \quad f_{\mu,\kappa}^S(r) = r^{l^S} e^{-\zeta_\mu r^2}, \quad l^S = l-1 = \kappa - 1, \quad l > 0, \tag{57}$$

which is a linear combination of functions with $n^S = l^S + 1 = l = n - 1$ and $n^S = l^S + 3 = l + 2 = n + 1$, respectively. Specifically, a $2p_{1/2}$ function is to be kinetically balanced by a fixed combination of a $1s_{1/2}$ function and a $3s_{1/2}$ function, $3d_{3/2}$ by $2p_{3/2}$ and $4p_{3/2}$, and $4f_{5/2}$ by $3d_{5/2}$ and $5d_{5/2}$, and so on. The spinor-UKB prescription amounts just to taking the two functions in Eq. 57 multiplied by $\Omega_{-\kappa,m_j}(\vartheta,\varphi)$ as independent functions for the small component. That is, a spinor-UKB basis coincides with the RKB basis when $\kappa < 0$ and differs from the latter only in the radial parts in the small component when $\kappa > 0$.

In the scalar-UKB prescription, one starts with scalar Cartesian Gaussians of angular momentum l for the large component, i.e., $g_\mu = x^i y^j z^k e^{-\zeta_\mu r^2}$ $(i+j+k=l)$, and takes their derivatives for the small component. When transformed to spherical Gaussians, the latter consist of two sets of functions of angular momentum $l-1$, one of $n^S = l = l^S + 1$ and the other of $n^S = l+2 = l^S + 3$. The former results directly from the differentials over $x^i y^j z^k$ in g_μ, whereas the other from the transformation of the $l+1$ Cartesian to spherical Gaussians. The two sets of functions can be combined according to Eq. 57 to facilitate the construction of spinors. After discarding linearly dependent functions, the resultant j-adapted UKB basis will consist of both $j = l - 1/2$ and $j = l + 1/2$ spinors for both the large and small components. For instance, a $3d$-type Cartesian Gaussian function of exponent ζ_μ gives rise to $3d_{3/2}$ and $3d_{5/2}$ spinor functions for the large component, and $4f_{5/2}$, $4f_{7/2}$, $5\times 2\tilde{p}_{1/2} - 2\zeta_\mu \times 4\tilde{p}_{1/2}$, and $5\times 2\tilde{p}_{3/2} - 2\zeta_\mu \times 4\tilde{p}_{3/2}$ spinor functions for the small component. The particular notation of $n\tilde{p}_j$ (instead of np_j) for the spinor functions is to emphasize that they are not normalized. Generally, for states of $\kappa < 0$, scalar-UKB differs from RKB if the large-component basis consists simultaneously of functions of angular momenta l and $l+2$. So is the case for states of $\kappa > 0$ if the large-component basis consists simultaneously of functions of angular momenta l and $l-2$. A direct deduction is that the scalar-UKB and RKB are actually identical for $p_{1/2}$ type of states since there are no functions of $l - 2 = -1$. Note that the present scalar-UKB prescription is somewhat different from that widely used in the literature. The latter usually does not make the j-adaptation

such that the scalar-UKB basis itself does not transform as the basis of irreducible representations of double point groups or of time reversal symmetry. Both symmetries can only be recovered later on in the self-consistent field algorithm. In contrast, the present scalar-UKB amounts to directly generating symmetrized integrals. However, such a difference resides only in the implementation and efficiency, not in the calculated results.

The number of j-adapted spherical Gaussian-type basis functions for the large and small components in the RKB, spinor-UKB and scalar-UKB descriptions can be counted according to the expressions given in Table 1. Taking a standard all-electron basis $30s26p15d10f4g$ (in total 289 scalar functions) as an example, we have $N^L = 187$, $M^L = 102$, $N^S = 234$ and $M^S = 374$. The number of NES concomitant with 374 PES of $\kappa < 0$ is therefore $2N^L = 374$ for both the RKB and spinor-UKB, where it is $2N^S = 468$ for the scalar-UKB, leading to 94 unphysical solutions having a zero kinetic energy and clustering around $-2mc^2$. The situation is even worse for states of $\kappa > 0$: The RKB gives rise to $2M^L = 204$ NES, whereas the spinor- and scalar-UKB lead to 408 and 748 NES, respectively. In summary, the total number of the scalar-UKB basis functions is in this case 1.55 times that of the RKB, resulting in much enhanced danger of linear dependence. The statistics for the scalar-UKB is even worse when working with a Cartesian basis.

To further elucidate the relationship between the RKB and UKB prescriptions, we can decompose an UKB spinor ψ_i^{UKB} as

$$\psi_i^{\mathrm{UKB}} = \phi_i^R + \phi_i^r, \tag{58}$$

$$\phi_i^R = P_{\mathrm{RKB}}\psi_i^{\mathrm{UKB}}, \quad P_{\mathrm{RKB}} = \sum_p |\psi_p^{\mathrm{RKB}}\rangle\langle\psi_p^{\mathrm{RKB}}|, \tag{59}$$

$$\phi_i^r = P_{\mathrm{res}}\psi_i^{\mathrm{UKB}}, \quad P_{\mathrm{res}} = 1 - P_{\mathrm{RKB}}. \tag{60}$$

The composition of each RKB spinor ψ_p^{RKB} in ψ_i^{UKB} is then given by

$$C_{pi}^R = \langle\psi_p^{\mathrm{RKB}}|\psi_i^{\mathrm{UKB}}\rangle. \tag{61}$$

Table 1 Number of j-adapted spherical Gaussian basis functions for the large and small components in the RKB, spinor-, and scalar-UKB prescriptions

Large	RKB		Spinor-UKB		Scalar-UKB	
	Large	Small	Large	Small	Large	Small
$\kappa < 0$	$2N^L$	$2N^L$	$2N^L$	$2N^L$	$2N^L$	$2N^S$
$\kappa > 0$	$2M^L$	$2M^L$	$2M^L$	$4M^L$	$2M^L$	$2M^S$

n_l: Number of radial functions of angular momentum l for the large component; $N^L = \sum_{l=0}(l+1)n_l$; $M^L = \sum_{l=1} ln_l$; $N^S = n_0 + 2M^L$; $M^S = 2N^L$

If the absolute value of C_{pi}^R is close to 1, ψ_i^{UKB} is just a pure RKB spinor ψ_i^{RKB}.

The nuclear magnetic shielding [39] σ_{UKB} calculated in terms of an UKB basis can accordingly be decomposed into three terms,

$$\sigma_{\mathrm{UKB}} = 2\Re\sum_a \frac{\langle\psi_i^{\mathrm{UKB}}|D^{01}|\psi_a^{\mathrm{UKB}}\rangle\langle\psi_a^{\mathrm{UKB}}|D^{10}|\psi_i^{\mathrm{UKB}}\rangle}{\epsilon_i - \epsilon_a} \tag{62}$$

$$= \sigma_{(\mathrm{RKB})} + \sigma_{(\mathrm{res})} + \sigma_{(\mathrm{coup})}, \tag{63}$$

$$\sigma_{(\mathrm{RKB})} = 2\Re\sum_a \frac{\langle\psi_i^{\mathrm{UKB}}|D^{01}|\phi_a^R\rangle\langle\phi_a^R|D^{10}|\psi_i^{\mathrm{UKB}}\rangle}{\epsilon_i - \epsilon_a}, \tag{64}$$

$$\sigma_{(\mathrm{res})} = 2\Re\sum_a \frac{\langle\psi_i^{\mathrm{UKB}}|D^{01}|\phi_a^r\rangle\langle\phi_a^r|D^{10}|\psi_i^{\mathrm{UKB}}\rangle}{\epsilon_i - \epsilon_a}, \tag{65}$$

$$\begin{aligned}\sigma_{(\mathrm{coup})} = {} & 2\Re\sum_a \frac{\langle\psi_i^{\mathrm{UKB}}|D^{01}|\phi_a^R\rangle\langle\phi_a^r|D^{10}|\psi_i^{\mathrm{UKB}}\rangle}{\epsilon_i - \epsilon_a} \\ & + 2\Re\sum_a \frac{\langle\psi_i^{\mathrm{UKB}}|D^{01}|\phi_a^r\rangle\langle\phi_a^R|D^{10}|\psi_i^{\mathrm{UKB}}\rangle}{\epsilon_i - \epsilon_a},\end{aligned} \tag{66}$$

$$D^{01} = c\vec{\alpha}\cdot\vec{A}^{01}, \quad D^{10} = c\vec{\alpha}\cdot\vec{A}^{10}, \tag{67}$$

where ψ_i^{UKB} and ψ_a^{UKB} are the field-free occupied and unoccupied bispinors with energies ε_i and ε_a, respectively. $\vec{A}^{01}$ and $\vec{A}^{10}$ are the respective vector potentials due to the nuclear magnetic point dipole moment and the external magnetic field. For brevity, we have only considered the decomposition of the unoccupied bispinors.

3 Results and discussion

To elucidate the performance of the various kinetic balances, suffice it to take a one-electron system such as Rn^{85+} as a representative. All the calculations were carried out with the BDF program package [40–44]. A value of 137.0359895 a.u. for the speed of light and a point nuclear charge distribution were used all the time. Both PES and NES are to be labeled by the symmetry of the upper components although it may be more appropriate to label NES according to the symmetry of the lower components.

The original DKB prescription [34] amounts to choosing the same radial functions for the g_μ (35) and f_μ (36) sets, i.e., $R_\mu^L = R_\mu^S$. In this case, the resultant matrix equation (37) satisfies charge conjugation symmetry and is therefore invariant under the replacements $\kappa \to -\kappa$, $\mathbf{V} \to -\mathbf{V}$, $\epsilon^D \to -\epsilon^D - 2mc^2\mathbf{I}$, and $(\mathbf{A}^D, \mathbf{B}^D)^T \to (\mathbf{B}^D, \mathbf{A}^D)^T$ [45]. Although such a choice appears to work for B-spline type of basis sets in conjunction with finite nuclear distributions [34], it cannot be adopted for, e.g., Gaussian functions in conjunction with a point-like nuclear distribution. For

instance, it amounts to using $(1s, 1p)$ [for (g_μ, f_μ)] Gaussian functions of the same exponents to describe $s_{1/2}$ type of states but the integrals are divergent due to the last term of Eq. 89. On the other hand, when (ns, np) $(n > 1)$ Gaussian functions are used to describe such states, variational collapse occurs, see Table 2. So is the case for $p_{1/2}$ type of states. It appears that the only convenient and possible choice is to use $(1s, 2p)$, $(2p, 1s)$, $(2p, 3d)$, and $(3d, 2p)$ Gaussian functions to describe the $s_{1/2}$, $p_{1/2}$, $p_{3/2}$, and $3d_{3/2}$ types of states, respectively. Then, the number of integrals to be evaluated in the DKB is double that in the RKB. When ns $(n > 1)$ Gaussians are used to describe the $1s_{1/2}$ state in the RKB prescription, terrible variational collapse also takes place, which cannot be cured by invoking a finite nuclear distribution. This is at first glance rather unexpected since ns $(n > 1)$ Gaussians can well describe the s states in the nrl. Since ns $(n > 1)$ Gaussians vanish at the position of the nucleus, they must be over peaked in the vicinity of the nucleus to mock up the singularities of the wave function. The corresponding small-component functions are even more over peaked. However, this is not the very reason for the observed collapse. Instead, the collapse is due to the fact that the '$(n-1)\tilde{p}$ minus $(n+1)\tilde{p}$' type of combinations lead to artificial radial nodes in the small component of $1s_{1/2}$. This then results in a considerable overestimate of the nuclear attraction, which cannot be compensated by the corresponding overestimate of the kinetic energy. In other words, the response of the nuclear attraction to the change in the basis set is a lot larger than that of the kinetic energy. A further evidence for the above elucidation is that the collapse disappears when the $(n-1)\tilde{p}$ or $(n+1)\tilde{p}$ components of the small-component functions are eliminated. However, this is no longer in the spirit of the RKB. This exercise reveals that the use of nl $(n = l+1, l = 0, 1, 2, \ldots)$ type of Gaussians in practical calculations is not only a matter of economy but also a must.

The energy levels of Rn^{85+} calculated with various basis sets are documented in Table 3. We start with an even-tempered basis set of $30s20p10d$. It turns out that the $30s$ functions are almost saturated such that the energy levels of the $ns_{1/2}$ states by the RKB, DKB, and scalar-UKB are very close to each other. As said before, the scalar-UKB and RKB are always identical for the $np_{1/2}$ states. They appear to yield the same results also for the $np_{3/2}$ states but this is because there are no f-functions in the basis set. The corresponding basis set for the IKB is $30p_{1/2}20s_{1/2}$ $20d_{3/2}10p_{3/2}$ of the same exponents as the $30s$, $20p$, $20p$,

Table 2 Energy levels (in a.u.) of Rn^{85+} calculated with various types of Gaussian basis sets

	RKB	Spinor-UKB	DKB				
			$n' = 1$	$n' = 2$	$n' = 3$	$n' = 4$	$n' = 5$
$1s_{1/2}$ (−4158.42442)							
$n = 1$	*−4158.42439*	−4158.42439		*−4158.42439*	−4158.42437	−4158.42451	−37564.38764
$n = 2$	−35926.99684	−35926.99684		−37565.80119	−37565.26225	−37564.79492	−37564.38764
$n = 3$	−36745.08235	−36745.08235		−3544.58979	−37565.26225	−37564.79492	−37564.38764
$n = 4$	−36803.10833	−36803.10833		−3530.16082	−3513.24935	−37564.79492	−37564.38764
$n = 5$	−36785.34283	−36785.34283		−3523.09945	−3501.97476	−3496.30026	−37564.38764
$2p_{1/2}$ (−1070.09528)							
$n = 2$	−1070.09518	−1070.09518	*−1070.09518*	−37565.79220	−37565.25445	−37564.78806	−37564.38157
$n = 3$	−1070.09490	−1070.09489	−1070.09489	−37565.79220	−37565.25445	−37564.78806	−37564.38157
$n = 4$	−1070.09356	−1070.09353	−1070.09354	−37565.79220	−37565.25445	−37564.78806	−37564.38157
$n = 5$	−1070.08776	−1070.08760	−7867.01351	−18522.49274	−37565.25445	−37564.78806	−37564.38157
$2p_{3/2}$ (−948.45140)							
$n = 2$	−948.45128	−948.45128		−948.45128	*−948.45128*	−948.45129	−948.45129
$n = 3$	−948.45102	−948.45102		−948.45102	−948.45102	−948.45101	−948.45102
$n = 4$	−948.44982	−948.44982		−948.44982	−948.44982	−948.44980	−948.44977
$n = 5$	−948.44502	−948.44502		−948.44503	−948.44504	−948.44503	−948.44495
$3d_{3/2}$ (−425.13636)							
$n = 3$	−425.13575	−425.13575		*−425.13575*	−425.13575	−37564.79491	−37564.38764
$n = 4$	−425.13522	−425.13522		−425.13522	−425.13522	−425.13522	−37564.38764
$n = 5$	−425.13333	−425.13333		−425.13333	−425.13333	−425.13333	−425.13334

n and n' are the respective principal quantum numbers for the large- and small-component functions, see Eq. 81. The exponents ζ_i are $0.02 \times 2.05^i, i = 0, \ldots, 49$. The combinations of lowest n and n' values are italicized. The analytic (exact) values are in parentheses

Table 3 Comparison of RKB, IKB, scalar-UKB, and DKB even-tempered Gaussian basis sets ($\alpha^{i-1} \times \beta, i = 1, \ldots n$) for the energy levels of Rn^{85+}

	RKB	IKB	DKB	UKB	DEQ
$30s20p10d$:	$\alpha_s = 2.05, \beta_s = 26.216, \alpha_p = 1.9, \beta_p = 122.62, \alpha_d = 1.8, \beta_d = 37.791$				
$1s_{1/2}$	−4158.42154	−4156.54567	−4158.42182	−4158.42154	−4158.42442
$2s_{1/2}$	−1070.09456	−1057.62114	−1070.09461	−1070.09456	−1070.09528
$3s_{1/2}$	−461.40880	−433.76384	−461.40881	−461.40880	−461.41101
$2p_{1/2}$	−1070.12657	−1070.09441	−1070.08237	−1070.12657	−1070.09528
$3p_{1/2}$	−438.40372	−500.16872	−438.40429	−438.40372	−461.41101
$2p_{3/2}$	−948.43557	−934.04051	−948.43553	−948.43557	−948.45140
$3p_{3/2}$	−388.03251	−299.83491	−387.92697	−388.03251	−425.13636
$3d_{3/2}$	−425.13408	−425.13521	−425.13424	−425.13216	−425.13636
$4d_{3/2}$	−234.85253	−248.34103	−234.85297	−234.85082	−238.62902
$40s25p15d$:	$\alpha_s = 2.05, \beta_s = 0.08405, \alpha_p = 1.9, \beta_p = 4.952, \alpha_d = 1.8, \beta_d = 2.0$				
$1s_{1/2}$	−4158.42346	−4158.42322	−4158.42356	−4158.42346	−4158.42442
$2s_{1/2}$	−1070.09498	−1070.09230	−1070.09499	−1070.09498	−1070.09528
$3s_{1/2}$	−461.40969	−461.40436	−461.40968	−461.40969	−461.41101
$2p_{1/2}$	−1070.08485	−1070.08344	−1070.08460	−1070.08485	−1070.09528
$3p_{1/2}$	−461.40713	−461.40692	−461.40717	−461.40713	−461.41101
$2p_{3/2}$	−948.45139	−948.44234	−948.45139	−948.45139	−948.45140
$3p_{3/2}$	−425.13627	−424.98201	−425.13627	−425.13627	−425.13636
$3d_{3/2}$	−425.13428	−425.13413	−425.13465	−425.13256	−425.13636
$4d_{3/2}$	−238.62764	−238.62803	−238.62787	−238.62658	−238.62902
$50s40p20d$:	$\alpha_s = 2.05, \beta_s = 0.02, \alpha_p = 1.9, \beta_p = 0.2, \alpha_d = 1.8, \beta_d = 2.0$				
$1s_{1/2}$	−4158.42439	−4158.42438	−4158.42439	−4158.42439	−4158.42442
$2s_{1/2}$	−1070.09514	−1070.09517	−1070.09514	−1070.09514	−1070.09528
$3s_{1/2}$	−461.40974	−461.41409	−461.40973	−461.40974	−461.41101
$2p_{1/2}$	−1070.09520	−1070.09520	−1070.09520	−1070.09520	−1070.09528
$3p_{1/2}$	−461.41091	−461.41104	−461.41091	−461.41091	−461.41101
$2p_{3/2}$	−948.45139	−948.45141	−948.45139	−948.45139	−948.45140
$3p_{3/2}$	−425.13628	−425.13653	−425.13628	−425.13628	−425.13636
$3d_{3/2}$	−425.13635	−425.13636	−425.13635	−425.13634	−425.13636
$4d_{3/2}$	−238.62892	−238.62915	−238.62892	−238.62891	−238.62902

DEQ: Analytic (exact) values

and $10d$ functions, respectively. It is seen that the energy levels by this IKB basis are too far off, except only for the $2p_{1/2}$ and $3d_{3/2}$ states. When steep functions are added in, no discernible changes are observed for all the four kinetic balances. Instead, when $10s5p5d$ flat functions are added in, leading to $40s25p15d$, the IKB results are much improved while the RKB, DKB, and scalar-UKB ones are changed only marginally. When $8s10p5d$ steep functions and $2s5p$ flat functions are further added in, leading to $50s40p20d$, the results by the four kinetic balances become virtually identical, as should be. Overall, the RKB, DKB, and scalar-UKB perform rather similarly for the PES, whereas the IKB is out of the trend and requires very different basis sets. The latter arises from the fact that the actions of $\vec{\sigma} \cdot \vec{p}$ on $2p_{1/2}$ and $3d_{3/2}$ functions generate linear combinations of $1s_{1/2}$ and $3s_{1/2}$ and of $2p_{1/2}$ and $4p_{1/2}$ functions, respectively. In contrast, the actions of $\vec{\sigma} \cdot \vec{p}$ on $1s_{1/2}$ ($2p_{3/2}$) functions will generate pure $2p_{1/2}$ ($3d_{3/2}$) functions but multiplied with the exponents. Both cases indicate that an IKB basis set should be more flat than the RKB one. As well known, kinetic balances do not guarantee the full variational safety. Depending very much on the construction of the large-component basis, some bounds failures (or prolapse [46]) of $O(c^{-4})$ may occur. More specifically, the RKB and UKB provide variational safety for states of $\kappa < 0$ (in the case of a point nuclear model) but not for those of $\kappa > 0$, whereas the IKB may lead to bounds failures for both types of states. In this regard, the DKB appears to be most robust: No bounds failures have ever been observed in the present course even

with artificially enhanced relativity by using a value of 13.7 a.u. for the speed of light. This feature stems from the equivalent treatment of the PES and NES. Anyway, such bounds failures will diminish when approaching to the basis set limit, as revealed here.

The relationship between the scalar-UKB and RKB eigenvectors can be analyzed according to Eqs. 58 and 61. For brevity, we only report the results by the $30s10d$ basis set. It is seen from Figs. 1 and 2 that there exists perfect one-to-one correspondence between the PES by the scalar-UKB and RKB. This is no longer the case for the NES as scalar-UKB generates $p_{1/2}$ and $p_{3/2}$ functions for the small components from both s and d functions, whereas the RKB generates $p_{1/2}$ ($p_{3/2}$) for the small components from s (d) functions alone. The NES by the scalar-UKB can actually be classified into three categories, one mainly of RKB components ($|C^R_{pi}|^2 > 0.7$), one of little RKB components ($|C^R_{pi}|^2 < 0.3$, to be called residuals), and the remaining heavy mixtures between the RKB and residual subspaces. For a better illustration, the three sets of NES are separated by two horizontal lines in the figures. Note that the three sets of NES get crossed in energy. The energetically lowest $s_{1/2}$ type of NES correspond to the pure RKB ones (Fig. 1), whereas the energetically lowest $d_{3/2}$ type of NES are instead pure residuals due to steep s-functions (Fig. 2). That is, only high-lying NES are varying degrees of mixtures between the RKB and residual subspaces.

As the NES are unbound, the quality of their finite basis representations can only be assessed by examining their contributions to some physical properties. One of the best candidates for this purpose is NMR shielding constants. There have been two classes of four-component approaches for evaluating shielding constants. One is the standard

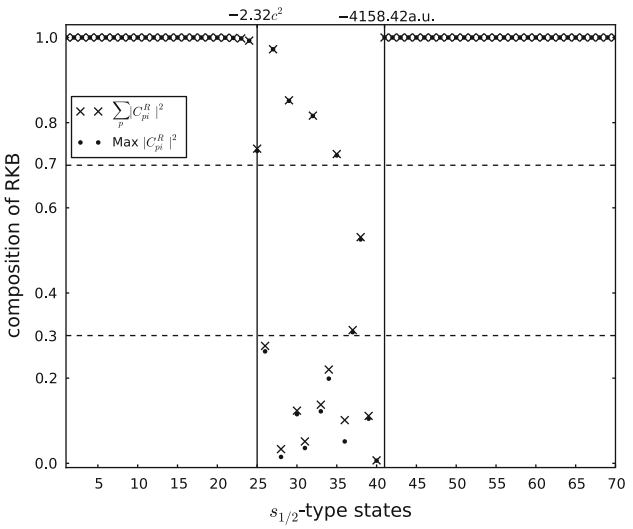

Fig. 1 Decomposition of the $s_{1/2}$ type of scalar-UKB spinors, see Eqs. 58 and 61

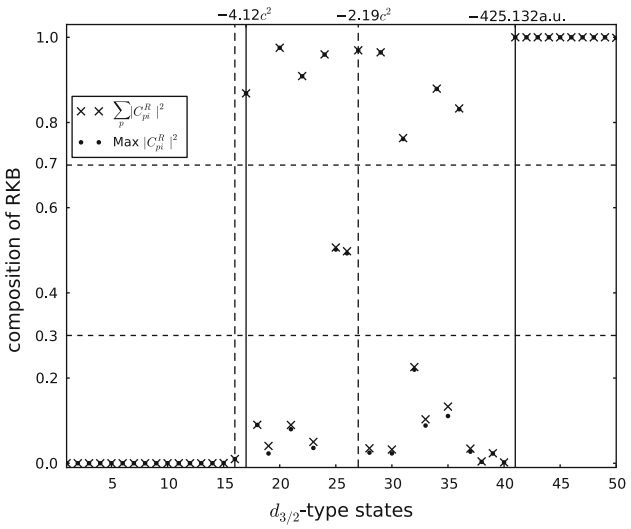

Fig. 2 Decomposition of the $d_{3/2}$ type of scalar-UKB spinors, see Eqs. 58 and 61

linear response theory (LRT) (62), which is only of a single term, the so-called paramagnetism. That is, the familiar diamagnetism known from the Ramsey non-relativistic theory [47] is 'missing'. This is due to the use only of a field-free basis or equivalently due to the lack of the magnetic balance. The 'missing' diamagnetism can be captured by incorporating explicitly the magnetic balance in various strictly equivalent ways [48–57]. For a recent critical analysis of such methods, we refer the reader to Ref. [52]. Here, we adopt only the restricted magnetic balance (RMB) for comparison, for it amounts to a direct generalization of the RKB to magnetic fields. For the ground state of Rn^{85+}, only s and d functions are needed to get a converged shielding according to group theory and their effects are additive [49]. The results calculated with various basis sets are given in Table 4. Although the IKB is expected to provide better descriptions of the NES than RKB, it is not really the case: The NES by the IKB and RKB have almost the same contributions to the shielding, irrespective of the basis set. As such, the IKB does not perform as well as the RKB due to inadequate representations of the PES. Although more involved, the DKB is not better than the RKB as well. What is really different is the scalar-UKB, which appears to account for the major effect of the NES even in the absence of d functions. This can well be understood according to the above analysis: The scalar-UKB can generate $p_{3/2}$ functions for the small components from the large-component s functions. In other words, the scalar-UKB can to some extent alleviate the heavy demands on high angular momentum functions [58]. However, this is only true for a Gaussian-type basis but not for, e.g., a Slater-type basis.

The individual contributions of the PES and NES to the shielding are further displayed in Figs. 3 and 4 for the $s_{1/2}$

Table 4 Comparison of RKB, IKB, scalar-UKB, spinor-UKB, and DKB even-tempered Gaussian functions ($\alpha^{i-1} \times \beta, i = 1, \ldots, n$) for the shielding constant (σ in ppm) of the ground state of Rn^{85+}

Basis	σ	RKB	IKB	DKB	Spinor-UKB	Scalar-UKB	RMB
30*s*:	$\alpha_s = 2.05, \beta_s = 26.216$						
	σ_d						1610.61
	σ_-	67.22	66.47	67.22	67.03	517.05	−9.88
	σ_+	4581.82	4563.22	4581.82	4584.03	4581.82	3585.19
	σ	4649.05	4629.69	4649.05	4651.06	5098.87	5185.91
30*s*10*d*:	$\alpha_s = 2.05, \beta_s = 26.216, \alpha_d = 1.8, \beta_d = 37.791$						
	σ_d						1610.61
	σ_-	486.71	488.44	492.61	484.49	489.10	−40.68
	σ_+	4652.14	4631.12	4649.50	4655.30	4643.10	3607.53
	σ	5138.86	5119.57	5142.10	5139.78	5132.20	5177.46
75*s*20*d*:	$\alpha_s = 2.05, \beta_s = 0.02; \alpha_d = 1.8, \beta_d = 2$						
	σ_d						1610.61
	σ_-	500.23	500.20	497.55	500.30	495.30	−48.55
	σ_+	4742.08	4741.88	4740.62	4742.19	4738.91	3681.42
	σ	5242.30	5242.08	5238.17	5242.48	5234.20	5243.48

σ_d: diamagnetism; σ_+ (σ_-): Contributions of positive (negative)-energy states to the paramagnetism; RMB: restricted magnetic balance. The analytic (exact) value [51] of σ is 5243.96 ppm

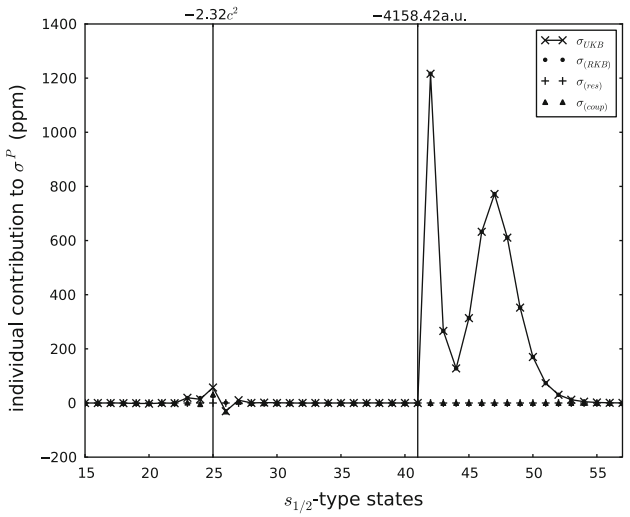

Fig. 3 Contributions of the $s_{1/2}$ type of states to the shielding of Rn^{85+}. The scalar-UKB 30*s*10*d* basis set result

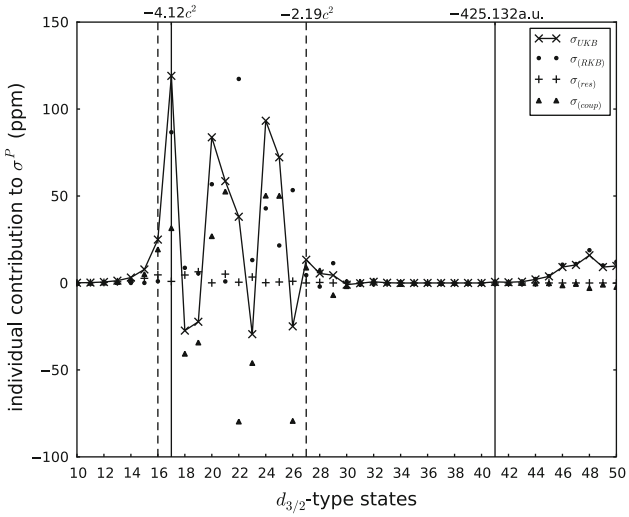

Fig. 4 Contributions of the $d_{3/2}$ type of states to the shielding of Rn^{85+}. The scalar-UKB 30*s*10*d* basis set result

and $d_{3/2}$ types of states, respectively. It is seen that the $s_{1/2}$ type of NES contribute very little. This results from cancelations between contributions from the large and small components [51]. On the other hand, it is those radially compact $s_{1/2}$ type of PES that make significant contributions. The opposite is true for the $d_{3/2}$ type of states. Only the radially compact NES of energies between $-4mc^2$ and $-2mc^2$ make significant contributions [51, 59]. Such states are either mainly of RKB components or of little RKB components (see Fig. 2). It is mainly the latter that makes the scalar-UKB and RKB different for the calculation of the shielding. In contrast, the pure residuals, i.e., the lowest NES arising from steep *s* functions, have no contributions. In the basis set limit, the 'extra' UKB terms $\sigma_{(res)}$ (65) and $\sigma_{(coup)}$ (66) will vanish such that the respective contributions of the PES and NES become identical with those by other schemes. However, such terms still survive even with a basis as large as 75*s*20*d*, see Table 5. In other words, the scalar-UKB performs better than the RKB for medium-sized Gaussian-type basis sets but does not converge faster to the basis set limit. The really effective approaches for reducing the basis set

Table 5 Decomposition of the shielding constant (in ppm) of the ground state of Rn^{85+} calculated by the UKB basis (cf. Eq. 63)

Shielding	Spinor-UKB				Scalar-UKB				RKB
	$\sigma_{(\mathrm{RKB})}$	$\sigma_{(\mathrm{res})}$	$\sigma_{(\mathrm{coup})}$	Sum	$\sigma_{(\mathrm{RKB})}$	$\sigma_{(\mathrm{res})}$	$\sigma_{(\mathrm{coup})}$	Sum	
30*s*:	$\alpha_s = 2.05, \beta_s = 26.216$								
σ_-	67.22	0.00	0.00	67.22	67.22	449.83	0.00	517.05	67.22
σ_+	4581.82	0.00	0.00	4581.82	4581.82	0.00	0.00	4581.82	4581.82
σ	4649.05	0.00	0.00	4649.05	4649.05	449.83	0.00	5098.87	4649.05
30*s*10*d*:	$\alpha_s = 2.05, \beta_s = 26.216, \alpha_d = 1.8, \beta_d = 37.391$								
σ_-	487.10	17.16	−11.65	492.61	487.30	34.30	−32.50	489.10	486.71
σ_+	4651.93	−0.03	−2.41	4649.50	4651.81	−0.14	−8.58	4643.10	4652.14
σ	5139.03	17.13	−14.06	5142.10	5139.12	34.16	−41.08	5132.20	5138.86
75*s*20*d*:	$\alpha_s = 2.05, \beta_s = 0.02; \alpha_d = 1.8, \beta_d = 2$								
σ_-	500.31	0.84	−3.61	497.55	500.34	1.19	−6.23	495.30	500.23
σ_+	4742.03	0.00	−1.40	4740.62	4742.01	−0.01	−3.09	4738.91	4742.08
σ	5242.34	0.84	−5.01	5238.17	5242.35	1.18	−9.33	5234.20	5242.30

For other explanations, see Table 4

requirements are those with explicit magnetic balances [48–57], as demonstrated by the RMB results in Table 4 and those more systematic investigations reported before [51]. Overall, the present investigations are complementary to the previous work [51], where the focus was on the various magnetic balances rather than the kinetic balances.

4 Conclusions

Various kinetic balances for four-component relativistic calculations are compared formally and assessed numerically. Neither the IKB nor the UKB is to be recommended, since the former has a serious drawback in that the correct nrl of positive-energy states cannot be guaranteed with a finite basis, while the latter tends to lead to much enhanced danger of linear dependence in the basis set. The DKB provides balanced descriptions of both positive- and negative-energy states and even full variational safety. However, such an advantage is largely offset by its complexity, given that it is still simpler than other schemes [5–7] that aim to achieve full variational safety. Overall, the RKB is the simplest ansatz and also an essential ingredient for formulating two-component relativistic theories. Therefore, the RKB should be regarded as the cornerstone of relativistic electronic structure calculations.

The negative-energy states of a Dirac-based mean-field Hamiltonian are part of the basis for properly representing physical properties. Although designed for potentially better representations of such states, neither the DKB nor the IKB offers any advantages over the RKB for calculations of, e.g., NMR parameters. The UKB is somewhat more effective in this regard. However, this is only true for a medium-sized Gaussian-type basis but not for, e.g., a Slater-type basis of any size. Even with a Gaussian basis, this particular advantage of UKB holds only for atomic or nearly atomic systems. The ultimate way for handling magnetic properties is to incorporate the magnetic balance in one way or another [48–57]. Then, the magnetic field-free calculations can be performed simply with the RKB. For calculations of tiny quantities such as quantum electrodynamics and parity non-conserving effects, the DKB may be adopted for its complexity is only minor compared to the high precision to be achieved. If one wants to solve the Dirac equation self-consistently for strong magnetic fields, the RMB or DMB (dual MB) will be the right choice. They amounts to replacing $\vec{\sigma} \cdot \vec{p}$ with $\vec{\sigma} \cdot (\vec{p} + \vec{A})$ in Eqs. 17 and 40, respectively.

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Appendix: The radial Dirac equation for a hydrogenic ion in a DKB Gaussian basis

The radial parts of the DKB basis functions (35) and (36) can be rewritten as

$$R^L_\mu(r) = \frac{1}{r}\pi^L_\mu(r), \quad R^S_\mu(r) = \frac{1}{r}\pi^S_\mu(r), \quad \mu = 1, \ldots, N, \quad (68)$$

such that the radial parts $(P_{n\kappa}(r), Q_{n\kappa}(r))^T = (\frac{1}{r}P'_{n\kappa}(r), \frac{1}{r}Q'_{n\kappa}(r))^T$ of spinor ψ_i (34) can be expanded as

$$\begin{pmatrix} P'_{n\kappa}(r) \\ Q'_{n\kappa}(r) \end{pmatrix} = \sum_{\mu=1}^{N} \begin{pmatrix} \pi_\mu^L \\ \frac{1}{2mc}\left(\frac{d}{dr}+\frac{\kappa}{r}\right)\pi_\mu^L \end{pmatrix} A^D_{\mu,n\kappa} + \sum_{\mu=1}^{N} \begin{pmatrix} \frac{1}{2mc}\left(\frac{d}{dr}-\frac{\kappa}{r}\right)\pi_\mu^S \\ \pi_\mu^S \end{pmatrix} B^D_{\mu,n\kappa}. \tag{69}$$

The matrix representation of the radial Dirac equation

$$\begin{pmatrix} V & c\left(-\frac{d}{dr}+\frac{\kappa}{r}\right) \\ c\left(\frac{d}{dr}+\frac{\kappa}{r}\right) & V-2mc^2 \end{pmatrix} \begin{pmatrix} P'_{n\kappa}(r) \\ Q'_{n\kappa}(r) \end{pmatrix} = \begin{pmatrix} P'_{n\kappa}(r) \\ Q'_{n\kappa}(r) \end{pmatrix} \epsilon^D \tag{70}$$

is then of the same form as Eq. 37 but with the matrix elements defined as

$$\mathbf{V}^{LL}_{\mu\nu} = \langle \pi_\mu^L | V | \pi_\nu^L \rangle, \tag{71}$$

$$\mathbf{V}^{SS}_{\mu\nu} = \langle \pi_\mu^S | V | \pi_\nu^S \rangle, \tag{72}$$

$$\mathbf{S}^{LL}_{\mu\nu} = \langle \pi_\mu^L | \pi_\nu^L \rangle, \tag{73}$$

$$\mathbf{S}^{SS}_{\mu\nu} = \left\langle \pi_\mu^S | \pi_\nu^S \right\rangle, \tag{74}$$

$$\begin{aligned} \mathbf{T}^{LL}_{\mu\nu} &= \frac{1}{2m}\left\langle \left(\frac{d}{dr}+\frac{\kappa}{r}\right)\pi_\mu^L \middle| \left(\frac{d}{dr}+\frac{\kappa}{r}\right)\middle|\pi_\nu^L \right\rangle \\ &= \frac{1}{2m}\left\langle \pi_\mu^L \middle| \left(-\frac{d^2}{dr^2}+\frac{\kappa(\kappa+1)}{r^2}\right)\middle|\pi_\nu^L \right\rangle, \end{aligned} \tag{75}$$

$$\begin{aligned} \mathbf{T}^{SS}_{\mu\nu} &= \frac{1}{2m}\left\langle \left(\frac{d}{dr}-\frac{\kappa}{r}\right)\pi_\mu^S \middle| \left(\frac{d}{dr}-\frac{\kappa}{r}\right)\middle|\pi_\nu^S \right\rangle \\ &= \frac{1}{2m}\left\langle \pi_\mu^S \middle| \left(-\frac{d^2}{dr^2}+\frac{\kappa(\kappa-1)}{r^2}\right)\middle|\pi_\nu^S \right\rangle, \end{aligned} \tag{76}$$

$$\mathbf{W}^{LL}_{\mu\nu} = \left\langle \left(\frac{d}{dr}+\frac{\kappa}{r}\right)\pi_\mu^L \middle| V \middle| \left(\frac{d}{dr}+\frac{\kappa}{r}\right)\pi_\nu^L \right\rangle, \tag{77}$$

$$\mathbf{W}^{SS}_{\mu\nu} = \left\langle \left(\frac{d}{dr}-\frac{\kappa}{r}\right)\pi_\mu^S \middle| V \middle| \left(\frac{d}{dr}-\frac{\kappa}{r}\right)\pi_\nu^S \right\rangle, \tag{78}$$

$$\begin{aligned} \mathbf{W}^{LS}_{\mu\nu} = \frac{1}{2mc}\Bigg[&\left\langle \pi_\mu^L \middle| V \middle| \left(\frac{d}{dr}-\frac{\kappa}{r}\right)\pi_\nu^S \right\rangle + \left\langle \left(\frac{d}{dr}+\frac{\kappa}{r}\right)\pi_\mu^L \middle| V \middle| \pi_\nu^S \right\rangle \\ &+ \frac{1}{2m}\left\langle \left(\frac{d}{dr}+\frac{\kappa}{r}\right)\pi_\mu^L \middle| \left(\frac{d}{dr}+\frac{\kappa}{r}\right)\middle| \left(\frac{d}{dr}-\frac{\kappa}{r}\right)\pi_\nu^S \right\rangle \Bigg], \end{aligned} \tag{79}$$

$$\begin{aligned} \mathbf{W}^{SL}_{\mu\nu} = \frac{1}{2mc}\Bigg[&\left\langle \pi_\mu^S \middle| V \middle| \left(\frac{d}{dr}+\frac{\kappa}{r}\right)\pi_\nu^L \right\rangle + \left\langle \left(\frac{d}{dr}-\frac{\kappa}{r}\right)\pi_\mu^S \middle| V \middle| \pi_\nu^L \right\rangle \\ &+ \frac{1}{2m}\left\langle \left(\frac{d}{dr}-\frac{\kappa}{r}\right)\pi_\mu^S \middle| \left(-\frac{d}{dr}+\frac{\kappa}{r}\right)\middle| \left(\frac{d}{dr}+\frac{\kappa}{r}\right)\pi_\nu^L \right\rangle \Bigg]. \end{aligned} \tag{80}$$

Note that the element for the above integrals is dr instead of r^2dr. For Gaussian-type functions (52), i.e.,

$$\begin{aligned} \pi_\mu^L &= r^n e^{-\zeta_\mu r^2}, \quad n \geq 1, \\ \pi_\nu^S &= r^{n'} e^{-\zeta_\nu r^2}, \quad n' \geq 1, \end{aligned} \tag{81}$$

the integrals are to be evaluated as

$$\mathbf{V}^{LL}_{\mu\nu} = -Z\mathcal{I}(2n-1,\zeta_{\mu\nu}), \quad \zeta_{\mu\nu} \doteq \zeta_\mu + \zeta_\nu, \tag{82}$$

$$\mathbf{V}^{SS}_{\mu\nu} = -Z\mathcal{I}(2n'-1,\zeta_{\mu\nu}), \tag{83}$$

$$\mathbf{S}^{LL}_{\mu\nu} = \mathcal{I}(2n,\zeta_{\mu\nu}), \tag{84}$$

$$\mathbf{S}^{SS}_{\mu\nu} = \mathcal{I}(2n',\zeta_{\mu\nu}), \tag{85}$$

$$\begin{aligned} \mathbf{T}^{LL}_{\mu\nu} = \frac{1}{2n'}[&4\zeta_\mu\zeta_\nu\mathcal{I}(2n+2,\zeta_{\mu\nu}) - 2(n+\kappa)\zeta_{\mu\nu}\mathcal{I}(2n,\zeta_{\mu\nu}) \\ &+ (n+\kappa)^2\mathcal{I}(2n-2,\zeta_{\mu\nu})], \end{aligned} \tag{86}$$

$$\begin{aligned} \mathbf{T}^{SS}_{\mu\nu} = \frac{1}{2n'}[&4\zeta_\mu\zeta_\nu\mathcal{I}(2n'+2,\zeta_{\mu\nu}) - 2(m-\kappa)\zeta_{\mu\nu}\mathcal{I}(2n',\zeta_{\mu\nu}) \\ &+ (n'-\kappa)^2\mathcal{I}(2n'-2,\zeta_{\mu\nu})], \end{aligned} \tag{87}$$

$$\begin{aligned} \mathbf{W}^{LL}_{\mu\nu} = -Z[&4\zeta_\mu\zeta_\nu\mathcal{I}(2n+1,\zeta_{\mu\nu}) - 2(n+\kappa)\zeta_{\mu\nu}\mathcal{I}(2n-1,\zeta_{\mu\nu}) \\ &+ (n+\kappa)^2\mathcal{I}(2n-3,\zeta_{\mu\nu})], \end{aligned} \tag{88}$$

$$\begin{aligned} \mathbf{W}^{SS}_{\mu\nu} = -Z[&4\zeta_\mu\zeta_\nu\mathcal{I}(2n'+1,\zeta_{\mu\nu}) - 2(n'-\kappa)\zeta_{\mu\nu}\mathcal{I}(2n'-1,\zeta_{\mu\nu}) \\ &+ (n'-\kappa)^2\mathcal{I}(2n'-3,\zeta_{\mu\nu})], \end{aligned} \tag{89}$$

$$\begin{aligned} \mathbf{W}^{LS}_{\mu\nu} = &-\frac{Z}{2mc}[-2\zeta_{\mu\nu}\mathcal{I}(n+n',\zeta_{\mu\nu}) + (n+n')\mathcal{I}(n+n'-2,\zeta_{\mu\nu})] \\ &-\frac{1}{4m^2c}[8\zeta_\mu\zeta_\nu^2\mathcal{I}(n+n'+3,\zeta_{\mu\nu}) \\ &-4((n+\kappa)\zeta_\nu^2 + (2n'+1)\zeta_\mu\zeta_\nu)\mathcal{I}(n+n'+1,\zeta_{\mu\nu}) \\ &+2((n'-1+\kappa)(n'-\kappa)\zeta_\mu + (n+\kappa)(2n'+1)\zeta_\nu) \\ &\times\mathcal{I}(n+n'-1,\zeta_{\mu\nu}) \\ &-(n+\kappa)(n'-1+\kappa)(n'-\kappa)\mathcal{I}(n+n'-3,\zeta_{\mu\nu})] \\ = &\mathbf{W}^{SL\dagger}, \end{aligned} \tag{90}$$

where

$$\begin{aligned} \mathcal{I}(n,\zeta_{\mu\nu}) &= \int_0^\infty r^n e^{-\zeta_{\mu\nu}r^2} dr = f_n \frac{(n-1)!!}{(2\zeta_{\mu\nu})^{(n+1)/2}}, \\ f_n &= \begin{cases} \sqrt{\pi} & n \in \text{non-negative even}, \\ 1 & n \in \text{non-negative odd}. \end{cases} \end{aligned} \tag{91}$$

Note that DKB also involves new integrals not present in other schemes when evaluating the NMR shielding constants. However, they are not to be presented here.

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