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Expectation values of operators in approximate two-component relativistic theories

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Abstract. Two methods for the evaluation of expectation values with approximate two-component relativistic functions are analysed. The first of them is based on the change of picture for the operator whose expectation value is to be calculated and associated with approximations leading to the given two-component relativistic wave function. This method, though hardly used in numerical calculations, gives the expectation values that directly reflect the accuracy of the wave function used for their calculation. The second method, most commonly used in calculations, neglects the picture change and is shown *always* to introduce an error of the order of α^2, where α is the fine structure constant. This error is present independently of the accuracy of the approximate two-component wave function. The perturbation formalism developed in this paper is illustrated by calculations of relativistic corrections to the expectation values of r^{-1} for arbitrary states of hydrogenic ions.

Key words: Relativistic quantum chemistry – Expectation values – Direct perturbation theory – Two-component relativistic Hamiltonians – Regular relativistic Hamiltonians

1 Introduction

It is commonly accepted that the true relativistic theory of many-electron systems should be derived from quantum electrodynamics (QED) [1] and based on the four-spinor representation of the electron-positron field operators. The lowest-order approximations to QED lead to commonly used Dirac-Coulomb (DC) and Dirac-Breit (DB) many-electron Hamiltonians [2, 3, 4] whose efficient implementations in atomic and molecular codes are already available [5, 6, 7, 8]. However, the prospect of routine four-component calculations for sizable molecules appears to be rather remote. This prompts a search for simplified relativistic methods of high credibility.

The main computational problems of the four-component relativistic methods in molecular calculations arise owing to the demand for the accurate enough representation [8, 9] of what is usually referred to as the small component of the Dirac four-spinor [10]. The truncated basis set expansion techniques may then lead to prohibitively large sizes even for relatively small systems. A solution to this problem can be achieved by passing from the four-component formalism to the two-component approximation, which is, as a matter of fact, a hidden way of handling the small component of four-spinors followed usually by some additional approximations.

The earliest attempt at relativity in terms of two-spinors was that of Pauli [11] and gives what is known as the Schrödinger-Pauli Hamiltonian, which is plagued by a number of unpleasant analytic features [10, 12, 13, 14]. A way to avoid or to circumvent the appearance of essentially singular operators, which arise in the case of the straightforward elimination of the small component [12, 13], has been proposed by Douglas and Kroll [15] and given a firm QED background in a series of papers by Sucher et al. [3, 4, 16]. This method was adapted for use in quantum chemistry of many-electron systems in the pioneering papers of the late Professor Almlöf et al. [17, 18, 19] and by Hess et al. [20, 21, 22] and made into a highly attractive and accurate computational tool by Hess and his co-workers [23]. Its success is mainly due to partial infinite summation of the relativistic perturbation series in α^2 ($\alpha = 1/c$ is the fine structure constant and c is the velocity of light, $c \approx 137.036\, a.u.$), which gives operators free of essential singularities. This is achieved through the initial unitary transform of the Dirac Hamiltonian [3, 4, 15, 19, 20, 24] by using the free-particle (fp) Foldy-Wouthuysen (FW) transformation [25].

Another possibility of using approximate regular relativistic Hamiltonians goes back to Durand et al. [26, 27] and Heully et al. [28] and has been more recently made into a successful computational tool by Snijders et al. [29, 30, 31]. When considered in their initial four-

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component form [32], the so-called regular approximation (RA) Hamiltonians [29, 30, 31] can be shown to follow from some FW transform of the Dirac Hamiltonian [33].

The spirit of the two-component theory prevails also in the case of the so-called direct perturbation theory (DPT) developed by Rutkowski [34] and by Kutzelnigg and his co-workers [12, 35, 36]. Owing to the use of the Sewell metric [37] the DPT approach permits the exact series expansions in powers of α^2 for operators, eigenenergies, and eigenfunctions. Thus, the DPT results can be used as a reference for qualifying other approximate methods of relativistic quantum chemistry.

The problem to be discussed in this paper relates to the calculation of the expectation value of operators other than the Hamiltonian. Obviously, performing any unitary transformation U on the Dirac Hamiltonian H_0 of a particle moving in some potential V [10, 24]:

$$H_0 = c\boldsymbol{\alpha p} + \beta c^2 + (V - c^2)I = \begin{pmatrix} V & c\boldsymbol{\sigma} p \\ c\boldsymbol{\sigma} p & V - 2c^2 \end{pmatrix}, \tag{1}$$

where I stands for a 4×4 unit matrix, will not affect the energy eigenvalues of the Dirac equation:

$$H_0 \Psi_0 = \epsilon_0 \Psi_0, \tag{2}$$

where the energy eigenvalue ϵ_0 is shifted by $-c^2$ with respect to the usual relativistic eigenenergy. In all equations presented in this paper we assume that atomic units are used.

The solution of the unitarily transformed eigenvalue problem:

$$H_0^U \Psi_0^U = \epsilon_0 \Psi_0^U, \tag{3}$$

where

$$H_0^U = U^\dagger H_0 U, \tag{4}$$

will give transformed solutions:

$$\Psi_0^U = U^\dagger \Psi_0. \tag{5}$$

Suppose now that the relativistic system described by the Hamiltonian (1) is affected by some external perturbation. For the sake of simplicity we assume that the perturbation operator, H^1, is fully diagonal and spin-independent, i.e.,

$$H^1 = q \times I, \tag{6}$$

where q is some one-electron operator, which may depend on the particle's coordinates and momenta. Thus, the perturbed Dirac Hamiltonian reads:

$$H(\mu) = H_0 + \mu H^1 = \begin{pmatrix} V + \mu q & c\boldsymbol{\sigma} p \\ c\boldsymbol{\sigma} p & V + \mu q - 2c^2 \end{pmatrix}, \tag{7}$$

and the parameter μ is used to order the perturbation series. The expectation value of the perturbation operator (6) in the state Ψ_0 follows then from the Hellmann-Feynman [38] theorem:

$$\langle \Psi_0 \mid H^1 \mid \Psi_0 \rangle \equiv \epsilon^1 = \left(\frac{\partial}{\partial \mu} \epsilon(\mu) \right)_{\mu=0}, \tag{8}$$

where $\epsilon(\mu)$ is the μ-dependent eigenvalue of the perturbed problem:

$$H(\mu)\Psi(\mu) = \epsilon(\mu)\Psi(\mu). \tag{9}$$

This is the result obtained prior to any transformations and/or approximations to the Dirac Hamiltonian. The equivalent result for ϵ^1 calculated with transformed four-component spinors (5) will be:

$$\begin{aligned} \epsilon^1 &= \langle \Psi_0^U \mid U^\dagger H^1 U \mid \Psi_0^U \rangle \\ &= \langle U\Psi_0^U \mid H^1 \mid U\Psi_0^U \rangle, \end{aligned} \tag{10}$$

i.e. the unitary transformation of the Hamiltonian will induce what is known as the change of 'picture' [25], which amounts to replacing H^1 by its unitary transform $U^\dagger H^1 U$ while using the transformed wave function Ψ_0^U. The second line of this expression says that if H^1 is used in its original non-transformed form, the wave function Ψ_0^U must be back transformed to the original representation. This means that the expectation value defined as:

$$\tilde{\epsilon}^1 = \langle \Psi_0^U \mid H^1 \mid \Psi_0^U \rangle \tag{11}$$

has no obvious relation to either (8) or (10). Although Eq. (10) is a trivial consequence of the matrix calculus, in quite a few cases the expectation values obtained from approximate relativistic schemes are calculated according to Eq. (11). Since the results obtained from Eq. (11) appear to be quite reasonable [23, 39], the error introduced by simultaneously using two different representations needs to be thoroughly investigated.

The relation between (8), (10) and (11) has recently been studied numerically by Kellö et al. [39]. Similar considerations were carried out much earlier by Baerends et al. [40] who investigated the relativistic atomic orbital contractions (expansions) and the proper way of defining them in terms of the expectation value of the coordinate operator in different pictures. One should also refer to numerous discussions with Professors Faegri Jr., Gropen, Hess, and Nieuwpoort during the Workshop held in Tromsø in 1992 [41]. The paper in its final shape benefitted from recent discussions with Professor Baerends and from comments by the unknown referee. The present study attempts to give the analysis of errors introduced by replacing either of Eqs. (8), (10) by Eq. (11). It will be shown that for the two-component approximate relativistic methods currently in use the error that follows from adopting Eq. (11) as a basis for the calculation of expectation values, is of the order of α^2. This will be done by first deriving the exact DPT relativistic corrections to non-relativistic expectation values of the operator q. Then, several other methods will be analysed by comparing their results with the exact DPT corrections.

2 Relativistic DPT corrections to expectation values

The so-called DPT of relativistic effects offers a general framework for the consideration of relativistic corrections to expectation values. It has been shown by Rutkowski [34] and Kutzelnigg [12] that by changing the metric from the usual one [10]:

$$\langle \Psi_0 \mid \Psi_0 \rangle = \langle \psi_0 \mid \psi_0 \rangle + \langle \chi_0 \mid \chi_0 \rangle = 1, \tag{12}$$

where ψ_0 and χ_0 denote the 'large' and 'small' components of Ψ_0 [10], respectively, to that of Sewell [37]:

$$\langle \overline{\Psi}_0 \mid \overline{\Psi}_0 \rangle = \langle \overline{\psi}_0 \mid \overline{\psi}_0 \rangle + \alpha^2 \langle \overline{\chi}_0 \mid \overline{\chi}_0 \rangle = 1, \tag{13}$$

i.e. by the transformation:

$$\Psi_0 = \begin{pmatrix} \psi_0 \\ \chi_0 \end{pmatrix} \Rightarrow \overline{\Psi}_0 = \begin{pmatrix} \overline{\psi}_0 \\ \overline{\chi}_0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & c \end{pmatrix} \begin{pmatrix} \psi_0 \\ \chi_0 \end{pmatrix}, \tag{14}$$

the Dirac equation can be written in a fully equivalent form:

$$\overline{H}_0 \overline{\Psi}_0 = \epsilon_0 S \overline{\Psi}_0. \tag{15}$$

The new operators entering the transformed Eq. (15) are defined by:

$$\overline{H}_0 = H^{00} + \alpha^2 H^{20} \tag{16}$$

$$S = S^{00} + \alpha^2 S^{20}, \tag{17}$$

where

$$H^{00} = \begin{pmatrix} V & \sigma p \\ \sigma p & -2 \end{pmatrix}, \quad H^{20} = \begin{pmatrix} 0 & 0 \\ 0 & V \end{pmatrix} \tag{18}$$

and

$$S^{00} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad S^{20} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \tag{19}$$

and make this equation manifestly expandable in the α^2 relativistic perturbation series, i.e.

$$\epsilon_0 = \epsilon^{00} + \alpha^2 \epsilon^{20} + \alpha^4 \epsilon^{40} + \ldots, \tag{20}$$

$$\psi_0 = \overline{\psi}^{00} + \alpha^2 \overline{\psi}^{20} + \alpha^4 \overline{\psi}^{40} + \ldots, \tag{21}$$

$$\chi_0 = \overline{\chi}^{00} + \alpha^2 \overline{\chi}^{20} + \alpha^4 \overline{\chi}^{40} + \ldots. \tag{22}$$

The 0^{th}-order solution, $\overline{\psi}^{00} = \psi^{00}$, for the large component of $\overline{\Psi}_0$ is the solution of the non-relativistic 2×2 Schrödinger equation:

$$h^{00} \psi^{00} = \epsilon^{00} \psi^{00}, \tag{23}$$

where

$$h^{00} = \frac{1}{2} p^2 + V. \tag{24}$$

By applying the same procedure to the perturbed Dirac's Eq. (9) one obtains the following counterpart of Eq. (15):

$$\overline{H}(\mu) \overline{\Psi}(\mu) = \epsilon(\mu) S \overline{\Psi}(\mu), \tag{25}$$

where

$$\overline{H}(\mu) = H^{00} + \mu H^{01} + \alpha^2 H^{20} + \alpha^2 \mu H^{21} \tag{26}$$

and

$$H^{01} = \begin{pmatrix} q & 0 \\ 0 & 0 \end{pmatrix}, \quad H^{21} = \begin{pmatrix} 0 & 0 \\ 0 & q \end{pmatrix}, \tag{27}$$

while Eqs. (20–22) are replaced by the corresponding double perturbation expansions involving solely even terms in α:

$$\epsilon = \epsilon(\alpha^2, \mu) = \epsilon^{00} + \mu \epsilon^{01} + \alpha^2 \epsilon^{20} + \alpha^2 \mu \epsilon^{21} + \alpha^4 \epsilon^{40} + \cdots, \tag{28}$$

$$\overline{\psi} = \overline{\psi}(\alpha^2, \mu) = \overline{\psi}^{00} + \mu \overline{\psi}^{01} + \alpha^2 \overline{\psi}^{20} + \alpha^2 \mu \overline{\psi}^{21} + \alpha^4 \overline{\psi}^{40} + \cdots, \tag{29}$$

$$\overline{\chi} = \overline{\chi}(\alpha^2, \mu) = \overline{\chi}^{00} + \mu \overline{\chi}^{01} + \alpha^2 \overline{\chi}^{20} + \alpha^2 \mu \overline{\chi}^{21} + \alpha^4 \overline{\chi}^{40} + \cdots. \tag{30}$$

By virtue of Eq. (28) the expectation value defined by (8) becomes:

$$\epsilon^1 = \epsilon^1(\alpha^2) = \epsilon^{01} + \alpha^2 \epsilon^{21} + \ldots, \tag{31}$$

where the leading term is the non-relativistic expectation value of the operator q,

$$\epsilon^{01} = \langle \overline{\psi}^{00} \mid q \mid \overline{\psi}^{00} \rangle = \langle \psi^{00} \mid q \mid \psi^{00} \rangle. \tag{32}$$

The *exact* α^2-order relativistic correction ϵ^{21} to the non-relativistic result (32) can be derived by using a double perturbation version of DPT [35] and reads:

$$\epsilon^{21} = 2\mathscr{R}e \langle \overline{\psi}^{00} \mid h^{20} \mid \overline{\psi}^{01} \rangle + \langle \overline{\psi}^{00} \mid h^{21} \mid \overline{\psi}^{00} \rangle, \tag{33}$$

where the 2×2 matrix operators h^{20} and h^{21} are defined by:

$$h^{20} = \frac{1}{4} \boldsymbol{\sigma p} (V - \epsilon^{00}) \boldsymbol{\sigma p}, \tag{34}$$

and

$$h^{21} = \frac{1}{4} \boldsymbol{\sigma p} (h^{01} - \epsilon^{01}) \boldsymbol{\sigma p}, \tag{35}$$

$$h^{01} = q. \tag{36}$$

The first-order perturbed function $\overline{\psi}^{01} = \psi^{01}$, i.e. correction to the large component arising from the external perturbation $H^{01}(q)$ follows from the usual perturbation expansion for the solution of the q-perturbed Schrödinger equation:

$$(h^{00} + \mu h^{01}) \overline{\psi}^0(\mu) = \epsilon^0(\mu) \overline{\psi}^0(\mu). \tag{37}$$

where $\overline{\psi}^0(\mu) = \psi^0(\mu)$ since Eq. (37) is of the zeroth-order in α^2. With the expansion:

$$\overline{\psi}^0(\mu) = \psi^0(\mu) = \overline{\psi}^{00} + \mu \overline{\psi}^{01} + \ldots = \psi^{00} + \mu \psi^{01} + \ldots, \tag{38}$$

one obtains the first-order solution of the form:

$$\overline{\psi}^{01} = R^{00} (q - \epsilon^{01}) \overline{\psi}^{00}, \tag{39}$$

where R^{00} is the reduced resolvent operator for the unperturbed Schrödinger equation:

$$R^{00} = \frac{P^{00}}{\epsilon^{00} - h^{00}} = \frac{1 - \mid \overline{\psi}^{00} \rangle \langle \overline{\psi}^{00} \mid}{\epsilon^{00} - h^{00}}. \tag{40}$$

The DPT expansion of the perturbed Dirac equation shows that the four-component problem can be, at least formally, reduced to the perturbation solution of the 2×2 μ-dependent equation of the form:

$$h(\alpha^2,\mu)\overline{\psi}(\alpha^2,\mu)=\epsilon(\alpha^2,\mu)\overline{\psi}(\alpha^2,\mu), \tag{41}$$

by means of the double perturbation expansion. The corresponding expansions of $\epsilon(\alpha^2,\mu)$ and $\overline{\psi}(\alpha^2,\mu)$ are given by Eqs. (28) and (29), respectively, and

$$h(\alpha^2,\mu)=h^{00}+\mu h^{01}+\alpha^2 h^{20}+\alpha^2\mu h^{21}+\ldots. \tag{42}$$

The higher-order terms of (42) can be derived by manipulating the initial perturbed Dirac equation according to the DPT scheme. One should point out that this is essentially a hidden way of handling the small component of the Dirac wave function. The problem of the appearance of essentially singular operators can be handled in a way devised by Kutzelnigg [42].

For the purpose of the present study the major advantage of the two-component Eqs (41, 42) and the resulting perturbed energy formulae of the form (33) is that they permit direct comparison of these *exact* results with those that follow from a variety of approximate two-component Hamiltonians. All of these two-component Hamiltonians can be expressed as given by Eq. (42) although the form of various perturbation terms in the corresponding $h(\alpha^2,\mu)$ operators will be in general different for different methods. Moreover, the DPT expansion leads to the presence of h^{21} (and of the corresponding operators of the higher order in α^2) directly in $h(\alpha^2,\mu)$. This results from including the perturbation operator in the Dirac Hamiltonian prior to any attempt to separate the large and small components. In other words, the expectation value of q which follows from the perturbation expansion of Eq. (41) reflects the change of 'picture' as expressed by Eq. (10). The same applies in the case of approximate two-component Hamiltonians; the presence of the counterpart of the $h^{21}, h^{41}, \ldots$ operators will depend on whether the change of picture is taken into account or not.

3 Expectation values in approximate two-component theories

3.1 Approximate two-component Hamiltonians and external perturbations

A two-component method M, derived from the Dirac theory under some additional assumptions, can be defined in terms of a two-component Hamiltonian h_M, which is assumed to be analytic in α^2, at least through the order of interest. In the absence of the external perturbation ($\mu=0$) such a Hamiltonian, $h_M(\alpha^2,0)$, can be written in terms of the expansion:

$$h_M(\alpha^2,0)=h^{00}+\alpha^2 h_M^{20}+\ldots, \tag{43}$$

where the leading term is assumed to be the non-relativistic Schrödinger Hamiltonian and h_M^{20} is a counterpart of h^{20} for the given approximate method M. In the presence of the external perturbation, which is included prior to any approximations leading from the Dirac Hamiltonian to (43), the same route will bring about the (α,μ)-dependent two-component Hamiltonian of the method M:

$$h_M(\alpha^2,\mu)=h^{00}+\mu h^{01}+\alpha^2 h_M^{20}+\alpha^2\mu h_M^{21}+\cdots. \tag{44}$$

By applying the double perturbation theory expansion to the eigenfunctions and eigenenergies of (44) one obtains the following counterpart of Eq. (31):

$$\epsilon_M^1=\epsilon_M^1(\alpha^2)=\epsilon^{01}+\alpha^2\epsilon_M^{21}+\cdots, \tag{45}$$

where ϵ^{01} is the non-relativistic result and

$$\epsilon_M^{21}=2\mathscr{R}e\langle\psi^{00}\mid h_M^{20}\mid\psi^{01}\rangle+\langle\psi^{00}\mid h_M^{21}\mid\psi^{00}\rangle. \tag{46}$$

As already mentioned the presence of h_M^{21} in (44) reflects the fact that the change of picture has been taken into account. However, given some approximate two-component method derived from the Dirac theory, one may consider discarding its two-component origin and add the external perturbation directly to (43). This is equivalent to neglecting the change of picture and treating the expectation value problem in the same way as in non-relativistic theories. The resulting μ-dependent Hamiltonian, $\tilde{h}_M(\alpha^2,\mu)$ will then be:

$$\tilde{h}_M(\alpha^2,\mu)=h^{00}+\mu h^{01}+\alpha^2 h_M^{20}+\ldots, \tag{47}$$

and will not contain any operators that would mix the external and relativistic perturbations, i.e. which would lead to operators of the h^{21} type. Nevertheless, the double perturbation expansion of the eigenvalue problem arising from the Hamiltonian (47) leads to:

$$\tilde{\epsilon}_M^1=\epsilon_M^1(\alpha^2)=\epsilon^{01}+\alpha^2\tilde{\epsilon}_M^{21}+\ldots, \tag{48}$$

with non-vanishing first-order relativistic correction $\tilde{\epsilon}_M^{21}$ given by:

$$\tilde{\epsilon}_M^{21}=2\mathscr{R}e\langle\psi^{00}\mid h_M^{20}\mid\psi^{01}\rangle. \tag{49}$$

It is of some interest to note that the result (49) can be alternatively defined in terms of μ-dependent non-relativistic solutions (37):

$$\tilde{\epsilon}_M^{21}=\left(\frac{\partial}{\partial\mu}\langle\psi^0(\mu)\mid h_M^{20}\mid\psi^0(\mu)\rangle\right)_{\mu=0}=2\mathscr{R}e\langle\psi^{00}\mid h_P^{20}\mid\psi^{01}\rangle. \tag{50}$$

This expresses the usual way of the calculation of relativistic corrections to non-relativistic expectation values by means of the numerical evaluation of the corresponding derivative [43, 44]. Let us stress that this result follows directly from the perturbation treatment of the Hamiltonian (47) obtained by adding *a posteriori* the external perturbation term to the unperturbed two-component Hamiltonian (43).

In what follows we shall consider two particular cases of the theory developed so far and derive expressions for deviations of ϵ_M^{21} and $\tilde{\epsilon}_M^{21}$ from the exact value of ϵ^{21} obtained in Sect. 2 by using the DPT approach. The first case is the calculation of relativistic corrections to expectation values in the so-called Pauli approximation ($M=P$) [10, 45]. It is of importance that several approximate two-component Hamiltonians have this approximation as the leading term of their α^2-expansion [3, 4, 20, 24]. Hence, all conclusions obtained for the Pauli approximation will be in general valid for a variety of other approximate Hamiltonians. The second case refers

to a series of two-component Hamiltonians of RA [31, 32] to the treatment of the Coulomb singularities. The lowest, 0^{th}-order, regular approximation (M = ZORA) [29, 30] does not, however, contain all terms of the α^2 order, i.e. the α^2-expansion of the ZORA Hamiltonian does not contain all terms of the Pauli operator. Thus, even the change of picture will not recover all terms of the DPT first-order relativistic correction (46) to the expectation value of h^{01}.

3.2 The Pauli approximation

The use of the Pauli approximation is one of the traditional ways [43, 44, 45, 46] of adding the first-order relativistic correction to expectation values of different operators. Let us first discuss the case when the picture change is taken into account. If one considers the external perturbation H^1 to the Dirac Hamiltonian prior to any approximation for the treatment of relativistic effects, the result becomes equivalent to that of DPT. Since within the present assumptions concerning H^1 the perturbation is just a modification of the external potential,

$$V \rightarrow V'(\mu) = V + \mu q, \tag{51}$$

one can derive the operators which enter Eq. (44) from the two-component μ-dependent Pauli Hamiltonian ($M = P$):

$$h_P(\alpha^2, \mu) = \frac{1}{2}p^2 + V' + \alpha^2 h_P^2(\mu) = h^{00} + \mu h^{01} + \alpha^2 h_P^2(\mu), \tag{52}$$

where

$$h_P^2(\mu) = \frac{1}{4}\boldsymbol{\sigma p} V' \boldsymbol{\sigma p} - \frac{1}{8}p^4 - \frac{1}{8}(p^2 V' + V' p^2). \tag{53}$$

Upon substituting V', one obtains:

$$h_P^2(\mu) = h_P^{20} + \mu h_P^{21}, \tag{54}$$

where

$$h_P^{20} = \frac{1}{4}\boldsymbol{\sigma p} V \boldsymbol{\sigma p} - \frac{1}{8}p^4 - \frac{1}{8}(p^2 V + V p^2) \tag{55}$$

is the usual Pauli operator for the system without additional perturbations, and

$$h_P^{21} = \frac{1}{4}\boldsymbol{\sigma p} q \boldsymbol{\sigma p} - \frac{1}{8}(p^2 q + q p^2). \tag{56}$$

As long as the non-relativistic reference state ψ^{00} and the non-relativistic first-order perturbed wave function ψ^{01} are the corresponding *exact* solutions [47], the ϵ_P^{21} correction, i.e. the first-order relativistic correction to the expectation value of the operator q calculated in the Pauli approximation:

$$\epsilon_P^{21} = 2\mathscr{R}e\langle\psi^{00} \mid h_P^{20} \mid \psi^{01}\rangle + \langle\psi^{00} \mid h_P^{21} \mid \psi^{00}\rangle, \tag{57}$$

is fully equivalent to the DPT result of Eq. (33). The corresponding proof is given in Appendix A. As indicated there, this proof strongly relies on the assumption that the exact non-relativistic solutions ψ^{00} and ψ^{01} are available.

The equivalence between ϵ_P^{21} and ϵ^{21} is a natural consequence of the change of 'picture' as expressed by Eq. (10) and accounted for by using V' in place of V in Eq. (53). Had we not taken the picture change into account, the corresponding equivalent of the two-component Hamiltonian (47) would have the form:

$$\tilde{h}_P(\alpha^2, \mu) = h^{00} + \mu h^{01} + \alpha^2 h_P^{20}, \tag{58}$$

and would lead to the following first-order relativistic correction to the expectation value of q:

$$\tilde{\epsilon}_P^{21} = 2\mathscr{R}e\langle\psi^{00} \mid h_P^{20} \mid \psi^{01}\rangle. \tag{59}$$

According to the formulae derived in Appendix A with the assumption of the exactness of both ψ^{00} and ψ^{01}, Eq. (59) differs from the DPT correction ϵ^{21} of Eq. (33):

$$\epsilon^{21} - \tilde{\epsilon}_P^{21} = \frac{1}{4}\left\langle\psi^{00} \mid \boldsymbol{\sigma p} q \boldsymbol{\sigma p} - \frac{1}{2}(p^2 q + q p^2) \mid \psi^{00}\right\rangle, \tag{60}$$

i.e. the difference will occur already in terms of the order of α^2 and will in general vanish only if $\boldsymbol{p}$ commutes with q. The non-zero value of the difference (60) is a consequence of not changing the 'picture' for the operator q.

The present considerations of the Pauli approximation have a more general character. It is rather common that the calculation of expectation values for different operators in approximate two- or one-component relativistic methods is based on the formalism borrowed from non-relativistic theories. Once the wave function, say $\Phi_M = \Phi_M(\alpha^2)$, obtained by some approximate two- or one-component relativistic method M, is known, the expectation value of the given (non-relativistic) operator Q is usually computed as $\langle\Phi_M \mid Q \mid \Phi_M\rangle$. The formal expansion of $\Phi_M(\alpha^2)$ into a power series in α^2 leads to expressions for relativistic corrections to the non-relativistic expectation value of Q, $\langle\Phi^0 \mid Q \mid \Phi^0\rangle$, where Φ^0 is the non-relativistic solution. It follows from derivations presented in this section that the expectation value $\langle\Phi_M \mid Q \mid \Phi_M\rangle$ will *always* differ from the exact DPT result already in terms of the order of α^2. The α^2-order error in (59) can only be removed by the change of 'picture', i.e. by replacing Q by its appropriate transformed counterpart.

3.3 The regular Hamiltonian approximations

The lowest (zeroth-) order Hamiltonian of the regular approximation (ZORA) [29, 30, 31] in the absence of the perturbation h^{01} can be derived by considering the 'metric perturbation' expansion [32] of the Dirac equation and reads:

$$h_{\mathrm{ZORA}} = h_{\mathrm{ZORA}}(\mu = 0) = V + \frac{1}{2}\boldsymbol{\sigma p}\mathscr{B}\boldsymbol{\sigma p}, \tag{61}$$

where

$$\mathscr{B} = \mathscr{B}(\alpha^2) = \frac{1}{1 - \frac{1}{2}\alpha^2 V} = 1 + \frac{1}{2}\alpha^2 \mathscr{B} V. \tag{62}$$

The change of picture can be achieved simply by adding the perturbation (6) to the Dirac Hamiltonian prior to approximations that result in the ZORA Hamiltonian [33], or equivalently, by using the substitution given by Eq. (51). Then,

$$h_{\mathrm{ZORA}}(\mu) = V' + \frac{1}{2}\boldsymbol{\sigma p}\frac{1}{1-\frac{1}{2}\alpha^2 V'}\boldsymbol{\sigma p} = h^{00} + \mu h^{01} + \alpha^2 h^{20}_{\mathrm{ZORA}} + \alpha^2\mu h^{21}_{\mathrm{ZORA}} + \ldots, \tag{63}$$

where

$$h^{20}_{\mathrm{ZORA}} = \frac{1}{4}\boldsymbol{\sigma p} V \boldsymbol{\sigma p} \tag{64}$$

and

$$h^{21}_{\mathrm{ZORA}} = \frac{1}{4}\boldsymbol{\sigma p} q \boldsymbol{\sigma p}. \tag{65}$$

The μ-dependent ZORA Hamiltonian acquires the mixed terms of the $\alpha^2\mu$ order and leads to the following form of the lowest order relativistic correction:

$$\epsilon^{21}_{\mathrm{ZORA}} = 2\mathscr{R}e\langle\psi^{00} \mid h^{20}_{\mathrm{ZORA}} \mid \psi^{01}\rangle + \langle\psi^{00} \mid h^{21}_{\mathrm{ZORA}} \mid \psi^{00}\rangle, \tag{66}$$

which can be converted into

$$\epsilon^{21}_{\mathrm{ZORA}} = 2\mathscr{R}e\langle\psi^{00} \mid h^{20} \mid \psi^{01}\rangle + \frac{1}{2}\epsilon^{00}\mathscr{R}e\langle\psi^{00} \mid p^2 \mid \psi^{01}\rangle + \frac{1}{4}\langle\psi^{00}\boldsymbol{\sigma p} q \boldsymbol{\sigma p} \mid \psi^{00}\rangle. \tag{67}$$

In spite of the change of picture for the perturbation operator h^{01}, this result differs from the exact DPT value of the correction, i.e.

$$\epsilon^{21} - \epsilon^{21}_{\mathrm{ZORA}} = -\frac{1}{2}\epsilon^{00}\mathscr{R}e\langle\psi^{00} \mid p^2 \mid \psi^{01}\rangle - \frac{1}{4}\epsilon^{01}\langle\psi^{00} \mid p^2 \mid \psi^{00}\rangle, \tag{68}$$

since neither h^{20}_{ZORA} nor h^{21}_{ZORA} are equivalent to the corresponding operators appearing in the DPT expansion. Moreover, let us also note that neither h^{20}_{ZORA} nor h^{21}_{ZORA} are equal to the operators h^{20}_P and h^{21}_P, respectively, obtained in the Pauli approximation [see Eqs. (55) and (56)]. This follows from the fact that the ZORA Hamiltonian does not contain all terms necessary for its reduction to the Pauli approximation [29, 30, 33]. This deficiency of the ZORA Hamiltonian is remedied by passing to the so-called first-order regular approximation (FORA) [29, 30, 33].

Once the one-electron ZORA eigenvalue problem in the absence of the external perturbation:

$$h_{\mathrm{ZORA}}\psi_{\mathrm{ZORA}} = \epsilon_{\mathrm{ZORA}}\psi_{\mathrm{ZORA}}, \tag{69}$$

is solved with the normalization condition $\langle\psi_{\mathrm{ZORA}} \mid \psi_{\mathrm{ZORA}}\rangle = 1$, one may try to evaluate the expectation value of h^{01} in the usual (non-relativistic) way, ignoring the fact that the two-component ZORA Hamiltonian follows from approximate treatment of the four-component equation. Then,

$$\tilde{\epsilon}^{1}_{\mathrm{ZORA}} = \langle\psi_{\mathrm{ZORA}} \mid h^{01} \mid \psi_{\mathrm{ZORA}}\rangle, \tag{70}$$

and, at least formally, can be expanded in a power series in α^2:

$$\tilde{\epsilon}^{1}_{\mathrm{ZORA}} = \tilde{\epsilon}^{01}_{\mathrm{ZORA}} + \alpha^2\tilde{\epsilon}^{21}_{\mathrm{ZORA}} + \cdots, \tag{71}$$

where by definition $\tilde{\epsilon}^{01}_{\mathrm{ZORA}} = \epsilon^{01}$ is the non-relativistic expectation value of h^{01} and

$$\tilde{\epsilon}^{21}_{\mathrm{ZORA}} = 2\mathscr{R}e\langle\psi^{00}_{\mathrm{ZORA}} \mid h^{01} \mid \psi^{20}_{\mathrm{ZORA}}\rangle, \tag{72}$$

with $\psi^{00}_{\mathrm{ZORA}} = \psi^{00}$ being the non-relativistic solution and $\psi^{20}_{\mathrm{ZORA}}$ obtained from the perturbation treatment of the α-expanded ZORA Hamiltonian (61) [33]:

$$h_{\mathrm{ZORA}} = h^{00} + \alpha^2 h^{20}_{\mathrm{ZORA}} + \cdots. \tag{73}$$

According to the derivations presented in Sect. 3.1, the double perturbation treatment of the Hamiltonian

$$\tilde{h}_{\mathrm{ZORA}}(\mu) = h_{\mathrm{ZORA}} + \mu h^{01} = h^{00} + \mu h^{01} + \alpha^2 h^{20}_{\mathrm{ZORA}} + \ldots, \tag{74}$$

which follows from the assumption that no picture change is involved, leads to the following equivalent of Eq. (72):

$$\tilde{\epsilon}^{21}_{\mathrm{ZORA}} = 2\mathscr{R}e\langle\psi^{00} \mid h^{20}_{\mathrm{ZORA}} \mid \psi^{01}\rangle, \tag{75}$$

where ψ^{01} is given by Eq. (39). It is important to note that, similarly to the Pauli-type Hamiltonian (58), the ZORA operator (74) will not involve terms which would mix the relativistic and h^{01} perturbations. By using the method described in Appendix A, one finds that $\tilde{\epsilon}^{21}_{\mathrm{ZORA}}$ will differ from the exact value ϵ^{21} obtained from the DPT expansion:

$$\epsilon^{21} - \tilde{\epsilon}^{21}_{\mathrm{ZORA}} = -\frac{1}{2}\epsilon^{00}\mathscr{R}e\langle\psi^{00} \mid p^2 \mid \psi^{01}\rangle + \frac{1}{4}\langle\psi^{00} \mid \boldsymbol{\sigma p}(q-\epsilon^{01})\boldsymbol{\sigma p} \mid \psi^{00}\rangle. \tag{76}$$

This difference arises from two different sources. One of them is that no change of picture is taken into account while defining the Hamiltonian (74). The second source follows from the incompleteness of the ZORA Hamiltonian in terms of the order of α^2.

The FORA Hamiltonian (see e.g. [33]) when expanded in the α^2 series contains all terms of the Pauli operator (55). Thus, all discussion of the Pauli approximation applies to the FORA Hamiltonian with the following consequences:

$$\epsilon^{21}_{\mathrm{FORA}} = \epsilon^{21}_P, \qquad \tilde{\epsilon}^{21}_{\mathrm{FORA}} = \tilde{\epsilon}^{21}_P \tag{77}$$

where the first equivalence corresponds to the 'change of picture', i.e. to the use of Eq. (51). The FORA correction $\epsilon^{21}_{\mathrm{FORA}}$ becomes therefore equal to the exact DPT result; differences between DPT and the FORA approximation will occur only in terms of the fourth- and higher-orders in α. The second equivalence in Eq. (77) arises when the perturbation μh^{01} is directly added to the FORA Hamiltonian. This is also the result that one obtains by expanding the expectation value of h^{01} in the FORA state ψ_{FORA},

$$\tilde{\epsilon}^1_{\mathrm{FORA}} = \langle \psi_{\mathrm{FORA}} \mid h^{01} \mid \psi_{\mathrm{FORA}} \rangle, \tag{78}$$

into the α^2 series:

$$\tilde{\epsilon}^{21}_{\mathrm{FORA}} = 2\mathscr{R}e\langle \psi^{00}_{\mathrm{FORA}} \mid h^{01} \mid \psi^{20}_{\mathrm{FORA}} \rangle, \tag{79}$$

where the wave function symbols are analogous to those used when discussing the ZORA approximation [see Eq. (72)] and the two-component FORA wave function is assumed to be normalized as $\langle \psi_{\mathrm{FORA}} \mid \psi_{\mathrm{FORA}} \rangle = 1$. The approximation expressed by Eq. (79) suffers from the use of h^{01} in the initial 'picture' and carries exactly the same error as the one present in $\tilde{\epsilon}^{21}_P$. Thus, one can conclude that the FORA expectation value of h^{01} (78) will always be in error already in terms of the order of α^2.

The FORA Hamiltonian certainly represents improvement over the ZORA approximation, for at least it contains all terms through the order of α^2. However, its form is definitely more cumbersome than that of the ZORA Hamiltonian. A hint at how to improve upon ZORA results without excessive effort follows from the consideration of the initial four-spinor, Ψ_{CPD-4} [32], whose large component is the ZORA wave function and the small component, χ_{ZORA}, is given by:[1]

$$\chi_{\mathrm{ZORA}} = \frac{1}{2}\alpha\mathscr{B}\boldsymbol{\sigma p}\psi_{\mathrm{ZORA}}, \tag{80}$$

and thus [32],

$$\Psi_{CPD-4} = \begin{pmatrix} \psi_{\mathrm{ZORA}} \\ \frac{1}{2}\alpha\mathscr{B}\boldsymbol{\sigma p}\psi_{\mathrm{ZORA}} \end{pmatrix}. \tag{81}$$

On considering (81) as an approximation to Dirac's four-spinor Ψ_0 of Eq. (14), one can approximate the expectation value (8) by

$$\begin{aligned} \epsilon^1_{CPD-4} &= \frac{\langle \Psi_{CPD-4} \mid H^1 \mid \Psi_{CPD-4} \rangle}{\langle \Psi_{CPD-4} \mid \Psi_{CPD-4} \rangle} \\ &= \frac{\langle \psi_{\mathrm{ZORA}} \mid h^{01} \mid \psi_{\mathrm{ZORA}} \rangle + \langle \chi_{\mathrm{ZORA}} \mid h^{01} \mid \chi_{\mathrm{ZORA}} \rangle}{\langle \psi_{\mathrm{ZORA}} \mid \psi_{\mathrm{ZORA}} \rangle + \langle \chi_{\mathrm{ZORA}} \mid \chi_{\mathrm{ZORA}} \rangle}. \end{aligned} \tag{82}$$

Upon expanding (82) into power series with respect to α^2, one obtains the first relativistic correction to ϵ^{01}:

$$\begin{aligned} \epsilon^{21}_{CPD-4} = {} & 2\mathscr{R}e\langle \psi^{00} \mid h^{01} \mid \psi^{20}_{\mathrm{ZORA}} \rangle \\ & + \left\langle \psi^{00} \mid \frac{1}{4}\boldsymbol{\sigma p}(h^{01} - \epsilon^{01})\boldsymbol{\sigma p} \mid \psi^{00} \right\rangle \end{aligned} \tag{83}$$

and

$$\epsilon^{21} - \epsilon^{21}_{CPD-4} = -\frac{1}{2}\epsilon^{00}\mathscr{R}e\langle \psi^{00} \mid p^2 \mid \psi^{01} \rangle. \tag{84}$$

The calculation of the expectation value by using Eq. (82) corresponds to renormalization of the ZORA solution and can be referred to as the scaled ZORA (s-ZORA) approach [30, 31, 49]. The same technique used for the total Dirac's Hamiltonian leads to the scaled expression for energy which gives the exact Dirac's energy for hydrogenic systems [49].

Yet another approximation related to (82) can be contemplated. From the definition of the expectation value ϵ^1_{CPD-4} we learn that the true four-spinor will involve normalization factor of the form $(\langle \psi_{\mathrm{ZORA}} \mid \psi_{\mathrm{ZORA}} \rangle + \langle \chi_{\mathrm{ZORA}} \mid \chi_{\mathrm{ZORA}} \rangle)^{-1/2}$. Thus, one can argue that the ZORA expectation value of h^{01} as given by Eq. (70) should be replaced by:

$$\tilde{\epsilon}^1_{s-\mathrm{ZORA}} = \frac{\langle \psi_{\mathrm{ZORA}} \mid h^{01} \mid \psi_{\mathrm{ZORA}} \rangle}{\langle \psi_{\mathrm{ZORA}} \mid \psi_{\mathrm{ZORA}} \rangle + \langle \chi_{\mathrm{ZORA}} \mid \chi_{\mathrm{ZORA}} \rangle}. \tag{85}$$

It is worthwhile pointing out that this definition of $\tilde{\epsilon}^1_{s-\mathrm{ZORA}}$ corresponds simply to the evaluation of the expectation value with *renormalized* ZORA density [49]. On expanding $\tilde{\epsilon}^1_{s-\mathrm{ZORA}}$ into a power series in α^2 one finds:

$$\begin{aligned} \epsilon^{21} - \tilde{\epsilon}^{21}_{s-\mathrm{ZORA}} = {} & -\frac{1}{2}\epsilon^{00}\mathscr{R}e\langle \psi^{00} \mid p^2 \mid \psi^{01} \rangle \\ & + \frac{1}{4}\langle \psi^{00} \mid \boldsymbol{\sigma p}q\boldsymbol{\sigma p} \mid \psi^{00} \rangle, \end{aligned} \tag{86}$$

which differs from the corresponding results for $\epsilon^{21}_{\mathrm{ZORA}}$ of Eq. (67) and ϵ^{21}_{CPD-4} of Eq. (84). Since the scaled ZORA expectation values as defined by Eq. (85) are essentially available as a by-product of standard ZORA calculations, any improvement over the result of the approximation (75) is worth investigating.

3.4 The Douglas-Kroll and related approximations

Over the past decade a great deal of attention has been given to what is called the Douglas-Kroll approximation [15], which has developed into one of the most powerful computational techniques of relativistic quantum chemistry [17, 20, 22]. The method has been analysed by Sucher et al. [3, 4, 16]. If the DK Hamiltonian is expanded into the α^2 series then the leading relativistic term corresponds to the Pauli approximation (55), which was analysed in Sect. 3.2 and Appendix A. Hence, the same conclusions as those reached for the Pauli approximation apply to the DK method.

It follows from our earlier considerations that once the DK expectation value of h^{01} is defined as the average of this operator,

$$\tilde{\epsilon}^1_{DK} = \langle \psi_{DK} \mid h^{01} \mid \psi_{DK} \rangle, \tag{87}$$

in DK state ψ_{DK}, which satisfies the μ-independent DK eigenvalue equation [3, 4, 15, 20], the error involved in this approximation occurs already in terms of the order of α^2 and is the same as that for the corresponding scheme within the Pauli approximation [see Eq. (60)]. This reflects again the fact that no 'picture' change has taken place while defining the expectation value by Eq. (87). The present conclusion concerning the error involved in calculations of $\tilde{\epsilon}^1_{DK}$ from Eq. (87) is at variance with the earlier analysis of the problem [39].

The inaccuracies involved in using the definition (87) can be removed by including the perturbation operator

[1] The four-component ZORA function is referred to by the Chang, Pélissier, and Durand approximation (CPD), which follows from treating the $\alpha^2\langle \overline{\chi}_0 \mid \overline{\chi}_0 \rangle$ term in Eq. (13) as a separate 'perturbation' [32]

h^{01} in the external potential V. This leads to a rather complicated form of the perturbation operator [39] in the new picture. Its use, however, guarantees that the relativistic corrections to ϵ^{01} will correspond to the same level of accuracy as that for the DK wave function. Obviously, the magnitude of the error resulting from the use of (87) will depend on the operator h^{01} and on nuclear charges of atoms in the given system. For h^{01}, operators, which assume large values far from nuclei, this error appears to be relatively small for atoms as heavy as gold ($Z = 79$) [39].

Recently a family of two-component relativistic operators h_{2k}, which are accurate through the α^{2k} order in the fine structure constant, has been derived [24]. None of them involve essentially singular operators and their α^{2k} expansion gives the Pauli approximation as the leading relativistic term. Thus, if ψ_{2k} is an eigenstate of h_{2k}, the expectation value, defined in analogy to (87), will carry an error of the order of α^2 in comparison with the exact DPT result. A remedy is provided by the replacement of V by V' in the given h_{2k} Hamiltonian, i.e. by the change of picture for the perturbation operator. This follows exactly the route described in Sect. 3.2 for the Pauli approximation. In comparison with the analogous procedure applied to the DK Hamiltonian [39], the h_{2k} operators in the presence of the external perturbation require only a redefinition of the h^{01} operator, which is replaced by relatively simple commutators [24].

4 A case study: the expectation value of the r^{-1} operator for hydrogenic ions

The conclusion that follows from the general treatment presented in Sects 2 and 3 is that all results obtained just by taking the average of the given operator over some approximate two- or one-component wave relativistic wave function will introduce certain error already in terms of the order of α^2. In some cases this can be avoided by transforming the operator in question into a new picture provided the method of approximation for relativistic effects is by itself accurate through terms of the order of α^2 in the wave function.

The use of the standard definition of expectation values without any reference to the changed picture is the easiest, most convenient, and fairly common way of performing their calculations. It is therefore worthwhile studying this problem in detail for an operator whose expectation value may be expected to be strongly affected by differences between methods used for its calculation. The r^{-1} operator satisfies this requirement because of the weak singularity whose presence makes, at least for deep core states, considerable difference between relativistic and non-relativistic expectation values. For present illustrative purposes, we consider a hydrogenic system with the nucleus of charge Z perturbed by a small term of the form μr^{-1}. Atomic units are used throughout this paper.

A general solution for the two-component non-relativistic problem with spin is well known to be (see e.g. [50]):

$$\psi^{00} \equiv \psi^{00}_{nj(ls),m_j} = N_{nl} F_{nl}(x) \mathscr{Y}_{j(ls),m_j}(\Omega, \sigma), \tag{88}$$

where $\mathscr{Y}_{j(ls),m_j}(\Omega, \sigma)$ is the spin and angular part depending on spherical angles $\Omega = (\theta, \phi)$ and spin σ. The radial part $F_{nl}(x)$, $x = (2Z/n)r$, is:

$$F_{nl}(x) = x^l e^{-x/2} L^{2l+1}_{n-l-1}(x), \tag{89}$$

with $L^{2l+1}_{n-l-1}(x)$ denoting the Laguerre polynomials [50, 51] and the normalization factor N_{nl} given by:

$$N_{nl} = \frac{2}{n^2} Z^{3/2} \sqrt{\frac{(n-l-1)!}{(n+l)!}}. \tag{90}$$

The non-relativistic eigenenergy corresponding to the state $\psi^{00}_{nj(ls),m_j}$ is $\epsilon^{00} \equiv \epsilon_{nj(ls)} \equiv \epsilon^{00}_n = -Z^2/2n^2$. The first-order perturbed wave function $\psi^{01} \equiv \psi^{01}_{nj(ls),m_j}$ for the μr^{-1} perturbation of the $\psi^{00}_{nj(ls),m_j}$ state reads:

$$\begin{aligned} \psi^{01}_{nj(ls),m_j} = {} & \frac{1}{Z} N_{nl} x^l e^{-x/2} \\ & \left\{ \left(-\frac{3}{2} - l + \frac{1}{2} x \right) L^{2l+1}_{n-l-1}(x) + x L^{2l+2}_{n-l-2}(x) \right\} \\ & \mathscr{Y}_{j(ls),m_j}(\Omega, \sigma) \end{aligned} \tag{91}$$

and the non-relativistic expectation value of r^{-1} is known [50] to be:

$$\epsilon^{01} \equiv \epsilon_{nj(ls)} \equiv \epsilon^{01}_n = \frac{Z}{n^2} \tag{92}$$

The *exact* first-order relativistic correction $\epsilon^{21}_{nj(ls)}$ obtained from the DPT approach is:

$$\begin{aligned} \epsilon^{21}_{nj(ls)} = {} & -\frac{3}{2}\frac{Z^3}{n^4} + \frac{Z^3}{n^3} \frac{1}{l + \frac{1}{2}} \\ & \left\{ 2 - \delta_{l,0} - \frac{j(j+1) - l(l+1) - s(s+1)}{l(l+1)} (1 - \delta_{l,0}) \right\} \end{aligned} \tag{93}$$

and depends on the quantum numbers l and s of the reference state and the coupling between the angular momenta $\mathbf{l}$ and $\mathbf{s}$, leading to the total angular momentum $\mathbf{j}$ with the associated quantum number $j = | l \pm \frac{1}{2} |$ [50]. This DPT result can be easily derived from the total relativistic energy expression for a hydrogenic system with the nuclear charge $Z - \mu$ [50]. In the case of the $l = 0$, i.e. $j = s = 1/2$ states, the DPT correction reduces to:

$$\epsilon^{21}_{n\frac{1}{2}(0\frac{1}{2})} = \frac{Z^3}{2n^4}(4n - 3). \tag{94}$$

Once the 'picture' change for the operator r^{-1} *is taken into account*, the Pauli [see Eq. (54)], FORA (see Sect. 3.3), DK, and all other approximations (see Sect. 3.4), whose leading term in the α^2 expansion is the Pauli operator, will give a result equal to ϵ^{21} of the DPT method, provided the exact solutions for ψ^{00} and ψ^{01} of the state under consideration are used. It should be pointed out that this statement automatically applies to all $h_{2k}, k = 1, 2, \ldots,$ Hamiltonians [24] discussed in

Section 3.4. Differences between the above-mentioned methods and their disagreement with the results of DPT will occur, depending on the method, in contributions of appropriately higher-order in α^2.

For methods whose α^2 expansion does not bring about the complete Pauli approximation in spite of the picture change, e.g. in the case of the ZORA scheme, the first-order relativistic correction turns out to be different from that given by Eq. (93). According to Eq. (68) the ϵ^{21} correction to the expectation value of the r^{-1} operator in the ZORA method differs from the DPT result by:

$$\epsilon^{21}_{nj(ls)} - \epsilon^{21}_{nj(ls),\mathrm{ZORA}} = -\frac{Z^3}{2n^4} \tag{95}$$

and the difference is independent of the angular quantum numbers. Similarly, calculating the expectation value of r^{-1} directly from the four-component ZORA/CPD (CPD-4) wave function leads to the following error in ϵ^{21} [see Eq. (84)]:

$$\epsilon^{21}_{nj(ls)} - \epsilon^{21}_{nj(ls),CPD-4} = -\frac{Z^3}{4n^4}. \tag{96}$$

It should be stressed that this result, which follows from the evaluation of the expectation value of H^1 of Eq. (6) according to Eq. (8) is compatible with the change of picture. The non-zero value of (96) indicates only that the CPD-4 wave function is an approximation to the true solution of the Dirac equation and carries some inaccuracies already in the order of α^2.

Of particular interest is the error involved in calculations of expectation values according to Eq. (11), i.e. without changing picture for h^{01} in spite of using two-component functions derived by approximate block-diagonalization (unitary transformation) of the initial Dirac Hamiltonian (12). The first-order relativistic corrections $\tilde{\epsilon}^{21}$ to ϵ^{01} derived in this paper lead to:

$$\epsilon^{21}_{nj(ls)} - \tilde{\epsilon}^{21}_{nj(ls),P} = \frac{1}{4}\frac{Z^3}{n^3}\frac{1}{l+\frac{1}{2}} \left\{\delta_{l,0} - \frac{j(j+1) - l(l+1) - s(s+1)}{l(l+1)}(1-\delta_{l,0})\right\}, \tag{97}$$

$$\epsilon^{21}_{nj(ls)} - \tilde{\epsilon}^{21}_{nj(ls),\mathrm{ZORA}} = -\frac{3}{4}\frac{Z^3}{n^4} + \frac{1}{4}\frac{Z^3}{n^3}\frac{1}{l+\frac{1}{2}} \left\{2 - \delta_{l,0} - \frac{j(j+1) - l(l+1) - s(s+1)}{l(l+1)}(1-\delta_{l,0})\right\}, \tag{98}$$

and

$$\epsilon^{21}_{nj(ls)} - \tilde{\epsilon}^{21}_{nj(ls),s-\mathrm{ZORA}} = -\frac{1}{2}\frac{Z^3}{n^4} + \frac{1}{4}\frac{Z^3}{n^3}\frac{1}{l+\frac{1}{2}} \left\{2 - \delta_{l,0} - \frac{j(j+1) - l(l+1) - s(s+1)}{l(l+1)}(1-\delta_{l,0})\right\}, \tag{99}$$

for the Pauli [see Eq. (60)], ZORA [see Eq. (76)], and scaled ZORA [see Eq. (86)] approximations, respectively. One should mention that the error introduced by using the expectation value definition with reference to h^{01} in the old picture [see Eq. (11)] within the context of the Pauli approximation will be exactly the same for all methods whose approximate relativistic Hamiltonians give the Pauli approximation as the leading term of the α^2 expansion. Thus, Eq. (97) applies also to the results calculated with wave functions resulting from the use of the FORA, DK, and h_{2k} Hamiltonians. The error in the relativistic correction to ϵ^{01} will therefore occur already in terms of the order of α^2 independently of how accurate the given approximation for a two-component wave function is.

It is also worthwhile noting that the use of the ϵ^{21} definitions, which comply with the change of picture, reflects directly the accuracy of approximate relativistic wave functions. For approximate wave functions studied in this paper, which involve inaccuracies in the order of α^2 (ZORA and CPD-4 functions), the α^2-order error in ϵ^{21} turns out to be independent of the angular part of the wave function and proportional to n^{-4}. When the expectation values are calculated by referring to the definition (11), the α^2-order error is found to depend, for methods considered in this paper, also on the angular part of the wave function and will affect the values of the spin-orbit contribution to the expectation value of r^{-1}. The leading contribution to this error will be proportional to n^{-3}, and hence, in general larger than that for methods compatible with the change of picture for h^{01}.

In the case of the $l = 0$ states the error formulae (97)–(99) simplify to:

$$\epsilon^{21}_{n\frac{1}{2}(0\frac{1}{2})} - \tilde{\epsilon}^{21}_{n\frac{1}{2}(0\frac{1}{2}),P} = \frac{1}{2}\frac{Z^3}{n^3}, \tag{100}$$

$$\epsilon^{21}_{n\frac{1}{2}(0\frac{1}{2})} - \tilde{\epsilon}^{21}_{n\frac{1}{2}(0\frac{1}{2}),\mathrm{ZORA}} = \frac{1}{4}\frac{Z^3}{n^4}(2n-3), \tag{101}$$

$$\epsilon^{21}_{n\frac{1}{2}(0\frac{1}{2})} - \tilde{\epsilon}_{n\frac{1}{2}(0\frac{1}{2}),s-\mathrm{ZORA}^{21}} = \frac{1}{2}\frac{Z^3}{n^4}(n-1). \tag{102}$$

These formulae show that for large enough values of n, the error in the first-order relativistic correction to ϵ^{01} resulting from the use of either of the three approximations is approximately equal to $Z^3/2n^3$ and makes about 25% of the exact DPT value of ϵ^{21} [see Eq. (94)]. This is to be compared with the large n behaviour of errors involved in $\epsilon^{21}_{nj(ls),ZORA}$ and $\epsilon^{21}_{nj(ls),CPD-4}$ given by Eqs. (95) and (96), respectively. For large n the relative value of these errors taken with respect to the DPT result (94) diminishes as n^{-1}. This is compatible with the fact that the relativistic contributions to the wave function diminish with the increase of the principal quantum number, thereby reducing the error introduced by the approximate way of passing from the four- to two-component representation.

The present illustration reflects some features of ϵ^{21} as calculated in different approximations for weakly-singular operator r^{-1}. The inaccuracies, which follow from either the use of Hamiltonians that do not produce the Pauli operator in their α^2 expansions or from the neglect of the change of picture for the operator of interest, will be even more important in the case of h^{01} with stronger singularities. However, their importance for non-singular h^{01} operators, which assume large values far from the

nucleus, will be diminished. This may explain the success of using Eq. (11) in approximate relativistic calculations of valence-determined properties like dipole or quadrupole moments [39]. The α^2-order error becomes than small enough that it can hardly be seen within the accuracy limits of the calculated expectation values.

5 Summary and conclusions

The first-order relativistic correction to the expectation value of some one-electron operator H^1 (h^{01}) has been derived for a variety of methods used in approximate two- or one-component relativistic calculations. Though quite obvious from the point of view of the route of derivation of these methods, the change of picture for H^1 (h^{01}) is usually neglected and its expectation values are evaluated according to Eq. (11). It has been shown that in such cases the error in the calculated relativistic contribution to $\tilde{\epsilon}^1$ occurs already in terms of the order of α^2 independently of the accuracy of the approximate two- or one-component relativistic wave function. The importance of this error for different two-component relativistic methods is illustrated by calculations for a hydrogenic system perturbed by r^{-1}.

The present analysis shows that the neglect of the picture change for operators in the evaluation of their expectation values may lead to considerable errors in $\tilde{\epsilon}^1$ as compared to the exact values given by DPT. The magnitude of these errors depends obviously on the form of h^{01} and the state under consideration. For deep core shells and (non-essentially) singular operators, the change of picture in the evaluation of their expectation values appears to be necessary. For non-singular operators and valence states the neglect of the change of picture will bring less significant errors in the calculated expectation values. Moreover, one has to take into account that most of the approximate two-component relativistic operators (ZORA, FORA, DK, h_{2k}) considered in this paper are based on a partial summation of the infinite operator series in α^2. Once the expectation value of h^{01} is obtained from Eq. (11) or equivalent expressions, the effect of higher-order terms is there and may lead to some *numerical* compensation of errors.

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Appendix A

Equivalence between the Pauli and DPT relativistic corrections to expectation values

As a matter of fact the equivalence between ϵ^{21} as given by the DPT expansion [see Eq. (33) of Sect. 2] and the result of the Pauli approximation (57) is the consequence of Eq. (10). However, it is useful and instructive to obtain this result algebraically, since some parts of the proof are used in the context of the analysis of other methods.

Let us note that the Pauli operator (55) can be rewritten in the form:

$$\begin{aligned} h_P^{20} &= \frac{1}{4}\boldsymbol{\sigma p} V \boldsymbol{\sigma p} - \frac{1}{8}(h^{00}p^2 + p^2 h^{00}) \\ &= \frac{1}{4}\boldsymbol{\sigma p} V \boldsymbol{\sigma p} - \frac{1}{8}[h^{00}p^2 - p^2(\epsilon^{00} - h^{00}) + \epsilon^{00}p^2]. \end{aligned} \tag{103}$$

If both ψ^{00} and ψ^{01} are the *exact* solutions of the zeroth- and first-order Schrödinger equations, respectively, i.e. if

$$h^{00}\psi^{00} \equiv \epsilon^{00}\psi^{00}, \tag{104}$$

and ψ^{01} is given by Eq. (39) with the reduced resolvent operator defined by Eq. (40), then

$$(\epsilon^{00} - h^{00}) \mid \psi^{01}\rangle = (1 - \mid \psi^{00}\rangle\langle\psi^{00} \mid)q \mid \psi^{00}\rangle, \tag{105}$$

and

$$\begin{aligned} 2\mathscr{R}e\langle\psi^{00} \mid h_P^{20} \mid \psi^{01}\rangle = {} & 2\mathscr{R}e\langle\psi^{00} \mid h^{20} \mid \psi^{01}\rangle \\ & + \frac{1}{8}\langle\psi^{00} \mid p^2 q + q p^2 \mid \psi^{00}\rangle \\ & - \frac{1}{4}\langle\psi^{00} \mid \boldsymbol{\sigma p}\epsilon^{01}\boldsymbol{\sigma p} \mid \psi^{00}\rangle. \end{aligned} \tag{106}$$

By substituting this result into Eq. (57) one finds:

$$\epsilon_P^{21} = 2\mathscr{R}e\langle\psi^{00} \mid h^{20} \mid \psi^{01}\rangle + \langle\psi^{00} \mid h^{21} \mid \psi^{00}\rangle = \epsilon^{21}, \tag{107}$$

where h^{20} and h^{21} are defined by Eqs. (34) and (36), respectively. Q.E.D.

This proof heavily relies on the assumption that both ψ^{00} and ψ^{01} are the *exact* non-relativistic solutions. Once this assumption becomes violated, as is often the case, the DPT result will differ from that of the Pauli approximation (57). It has already been pointed out by Kutzelnigg et al. [35, 42, 48] that the explicit use of the DPT formula (33) offers certain advantages and reduces the error carried out by the Pauli result ϵ_P^{21} for non-exact solutions of the Schrödinger equation. The accuracy of these two approaches has been recently analysed by one of the present authors [47].

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