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Theoretical
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Relativistic electron densities in the four-component Dirac representation and in the two-component picture

Hydrogen-like systems

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Abstract. Analytic formulae of the relativistic radial functions of hydrogen-like atoms in the four-component standard Dirac picture and in two approximations, (Pauli and ZORA), to the two-component (so-called Schrödinger or Newton–Wigner) picture and graphs of the respective relativistic changes of densities are presented and discussed. The two different pictures of the Dirac density of charge position and of the Newton–Wigner density of mass position are remarkably different in strongly inhomogeneous fields and result in respective differences in position-dependent expectation values, $\langle r^\nu \rangle$. The fractional magnitudes of $\Delta^{\mathrm{rel}}\langle r^\nu \rangle$, of $\Delta^{\mathrm{charge/mass}}\langle r^\nu \rangle$, and of the gauge dependence of ZORA (which for small n states is comparable to the difference of the two kinds of position observables) are all of order $Z^2\alpha^2$.

Key words: Relativistic quantum chemistry – Electron density – Hydrogen-like systems – Expectation values – Picture change

1 Introduction

Two approaches are common in relativistic quantum chemistry, both at the ab initio independent-particle or density functional levels and at the many-particle levels. These two approaches are the four-component spinor approach using the standard Dirac picture [1] and the two-component approach using the so-called Schrödinger or Newton–Wigner picture [2–5]. In general, two-component formalisms are difficult to obtain in closed form; therefore, some type of expansion is required, for instance, in terms of powers of the velocity of light or of the electromagnetic coupling constant. This is achieved by the Foldy–Wouthuysen transformation [6] or by the Regular Approximation (RA) [7–11], for instance.

In this letter we want to illustrate how strongly the two pictures differ concerning the electron density distribution function and also how well the densities converge as power series of α^2. With this aim, hydrogen-like orbitals are analyzed and displayed. The theoretical framework is reviewed in Sect. 2 and analytical formulae are communicated in Sect. 3. Diagrams and an analysis of the picture change of the electron density function and of some expectation values are given in Sect. 4.

2 Theoretical framework

In the "standard" representation of the four-component Dirac equation [1] for a single particle in the electric potential $W(\mathbf{r})$,

$$[\hat{H}^{\mathrm{D}} - E]\Psi^{\mathrm{D}} = \left[\hat{\beta}' mc^2 + \hat{\boldsymbol{\alpha}}\hat{\boldsymbol{p}}c + W(\mathbf{r}) - E\right]\Psi^{\mathrm{D}} = 0 \ , \tag{1}$$

$\mathbf{r}$ obviously has the meaning of the position of charge in ordinary space. Here $\hat{\beta}' = \hat{\beta} - 1$ is chosen so that electronic small energy states have $|E| \ll mc^2$. The other symbols have their usual meaning, with $\hat{\beta}' mc^2 + \hat{\boldsymbol{\alpha}}\hat{\boldsymbol{p}}c$ the kinetic mass energy in the Dirac picture. The electronic charge density distribution is then given by

$$\rho_e(\mathbf{r}) = \Psi^{\mathrm{D}^*}\Psi^{\mathrm{D}} = |\varphi|^2 + |\chi|^2\alpha^2 \ , \tag{2}$$

where the four-spinor Ψ^{D} is represented by the two two-spinors φ, χ:

$$\Psi^{\mathrm{D}} = \begin{pmatrix} \varphi \\ \alpha \cdot \chi \end{pmatrix} \ . \tag{3}$$

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Atomic units ($\hbar = 1$, $m_e = 1$, $4\pi\varepsilon_0 = 1$, $c = \alpha^{-1} \approx 137.036$) are used, α being Sommerfeld's fine structure constant.

Both the state functions, Ψ^D or φ, χ, and the energy, E, have convergent power expansions in α^2, at least for nonsingular potentials, W, for instance,

$$E = E^{(0)} + \alpha^2 E^{(1)} + \mathcal{O}(\alpha^4) \ , \tag{4}$$

$$\rho_e = |\varphi^{(0)}|^2 + \alpha^2 \left[2Re(\varphi^{(0)}\varphi^{(1)}) + |\chi^{(0)}|^2 \right] + \mathcal{O}(\alpha^4) \ , \tag{5}$$

where the nonrelativistic energy is

$$\begin{aligned} E^{(0)} &= 2Re\langle\chi^{(0)}|\hat{\boldsymbol{\sigma}}\hat{\boldsymbol{p}}|\varphi^{(0)}\rangle - 2m\langle\chi^{(0)}|\chi^{(0)}\rangle \\ &\quad + \langle\varphi^{(0)}|W|\varphi^{(0)}\rangle \\ &= 2T^{(0)} - T^{(0)} + W^{(0)} = T^{(0)} + W^{(0)} \end{aligned} \tag{6}$$

and $\varphi^{(0)}$ is the solution of the nonrelativistic Schrödinger equation

$$\left[\hat{T}^{(0)} + W - E^{(0)} \right] \varphi^{(0)} = 0 \ . \tag{7}$$

$\chi^{(0)} = \hat{\boldsymbol{\sigma}}\hat{\boldsymbol{p}}\varphi^{(0)}/2m$, and $\hat{T}^{(0)}$ is the nonrelativistic kinetic energy operator in the Schrödinger picture, $\hat{\boldsymbol{p}}^2/2m$. χ does not appear in the nonrelativistic approximation of $\mathcal{O}(\alpha^0)$ of the charge density $\rho_e^{(0)} = |\varphi^{(0)}|^2$ or in the respective expectation values such as the Coulomb potential energy $\langle -1/|\mathbf{r}| \rangle$ or the electric dipole moment $\langle e\,\mathbf{r} \rangle$. Therefore, it has been suggested to introduce a unitary transformation, U, of the relativistic equation (Eq. 1) to upper two-component form for electronic states, of the type [8]

$$\begin{aligned} &V^+ \left[\hat{H}^D - E \right] U \cdot U^+ \Psi^D = \\ &\quad \begin{bmatrix} \hat{T}^{(0)} + W + \Delta h - E & 0 \\ \bullet & \bullet \end{bmatrix} \begin{pmatrix} \tilde{\varphi} \\ 0 \end{pmatrix} = 0 \ , \end{aligned} \tag{8}$$

with $\tilde{\varphi} = \varphi^{(0)} + \mathcal{O}(\alpha^2)$ and $\Delta h = \mathcal{O}(\alpha^2)$. V^+ may be chosen as U^+. A general form of norm-conserving U, $U\ U^+ = 1$, is

$$U = \begin{pmatrix} 1/\sqrt{1 + XX^+} & 1/\sqrt{1 + XX^+} \cdot X \\ -1/\sqrt{1 + X^+X} \cdot X^+ & 1/\sqrt{1 + X^+X} \end{pmatrix} \ , \tag{9}$$

also with $U^+U = 1$, although $XX^+ \neq X^+X$ in general. The solution, $\tilde{\varphi}$, of the respective two-component relativistic wave equation

$$\left[\hat{T} + W + \Delta h - E \right] \tilde{\varphi} = 0 \tag{10}$$

yields the charge density $\rho(r)$ and the mass density $\tilde{\rho}(r')$,

$$\rho(r) = \tilde{\rho}(\mathbf{r}') = |\tilde{\varphi}(\mathbf{r}')|^2 \ , \tag{11}$$

where $\mathbf{r}' = U^+\mathbf{r}U = r + \varphi(\alpha^2)$. That is, $\tilde{\rho}(r') = |\tilde{\varphi}(\mathbf{r}')|^2$ is not the electric charge density in space $\mathbf{r}'$, but the probability density of the so-called average or particle or mass position, $\mathbf{r}'$. Accordingly, expectation values of type $\langle\tilde{\varphi}|\mathbf{r}^\lambda|\tilde{\varphi}\rangle$ have a modified meaning, which has been extensively discussed in the literature [2–5, 7, 11–16].

The transformation to Eq. (8) is achieved with X obeying the recursive relation (cf. Ref. [8])

$$2mc\ X = \hat{\boldsymbol{\sigma}}\hat{\boldsymbol{p}} - X\hat{\boldsymbol{\sigma}}\hat{\boldsymbol{p}}X - \alpha[X, W] \ . \tag{12}$$

Far from the nucleus, i.e. where $r \gg Z\alpha^2$, both $|V/mc^2|$ and $|\hat{\boldsymbol{\sigma}}\hat{\boldsymbol{p}}/mc|$ are small (with $\hat{\boldsymbol{\sigma}}\hat{\boldsymbol{p}}$ acting on a bound state function); then X also is small, $X \approx \hat{\boldsymbol{\sigma}}\hat{\boldsymbol{p}}/2mc$ and its α^2 expansion converges well. Near the nucleus, where $r \ll Z\alpha^2$, both $|V/mc^2|$ and $|\hat{\boldsymbol{\sigma}}\hat{\boldsymbol{p}}/mc|$ are large and $X = \mathcal{O}[(Z\alpha)^{\mathrm{sgn}(\kappa)}]$, where κ is the relativistic angular momentum quantum number, $\kappa = +1$ for $s_{1/2}$, -1 for $p_{1/2}$, $+2$ for $p_{3/2}$ etc. Then other types of expansions such as Douglas–Kroll–Hess (DKH) [17] or Chang–Pelissier–Durand (CPD/RA) [8, 9], and the RA [7, 10, 11] (zero-order ZORA, first order FORA, etc.) are appropriate.

The elimination of the small component of the Dirac equation yields

$$\left[W + \hat{\boldsymbol{\sigma}}\hat{\boldsymbol{p}} \frac{1}{2m + (E - W)\alpha^2} \hat{\boldsymbol{\sigma}}\hat{\boldsymbol{p}} - E \right] \varphi = 0 \ . \tag{13}$$

The Pauli or the α^2 approximation to ZORA (ZORA2) approaches correspond to suppressing $(E - W)/2mc^2$ or $E/(2mc^2 - W)$, respectively, in the denominator and then expanding in terms of α^2 and keeping the lowest order(s) only (and renormalizing in the Pauli case [18]). The fraction between the $\hat{\boldsymbol{\sigma}}\hat{\boldsymbol{p}}$s of Eq. (13) at the Dirac, Pauli, and ZORA levels is plotted in Fig. 1. Obviously the Pauli approximation breaks down in the strong-field region near the nucleus, whereas ZORA is a good approximation where the potential dominates, i.e. for $|W| \gg |E| > 0$. On the other hand, ZORA causes errors where $|E| > |W| > 0$, i.e. for large values of E and large r, see Fig. 1 and Ref. [19]. While ZORA works well for valence states with small $|E|$, it does not do so for $E \ll 0$ (deep core levels with small principal quantum numbers) or for $E \gg 0$ [19].

Figure 1 might suggest shifting the gauge zero of the potential W so that the energy of the state under

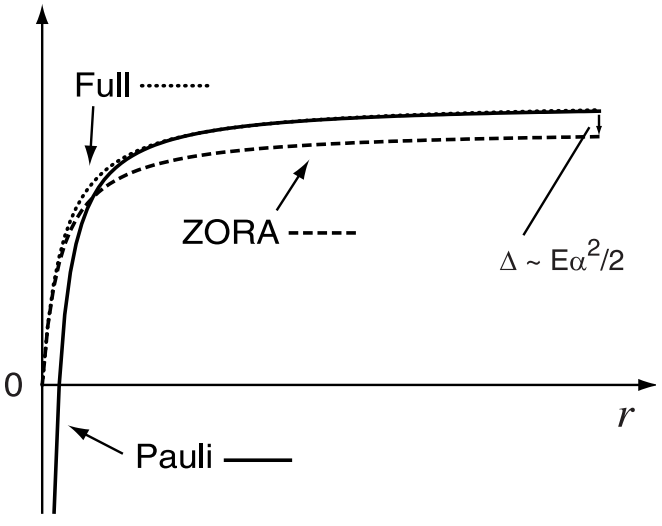

Fig. 1. The fraction in Eq. (13) and its ZORA and *Pauli* approximations, arbitrary units. Gauge of potential is $W \to 0$ for $r \to \infty$

discussion becomes zero, $W \to W - E_i$; however, the standard potential-energy zero is situated between the bound and the free states and thus yields an "unbiased" ZORA Hamiltonian. Choosing E_{1s} as the potential-energy zero would yield an exact ZORA energy for the 1*s* state, but the ZORA Hamiltonian as a whole would be biased with all states in the positive energy region (all Δs in Fig. 1 positive) and all eigenfunctions being even more incorrect, including $\tilde{\varphi}_{1s}^{\mathrm{ZORA}}$. Choosing $E_{n\kappa}$ as the potential-energy zero, the respective ZORA $\Delta\langle r^v\rangle_{\mathrm{m}}$ (m = mass) value of the $n\kappa$ state is obtained from $\varphi_{n\kappa}$ and is identical to or similar to the respective Dirac $\Delta\langle r^v\rangle_{\mathrm{c}}$ (c = charge) value, i.e. the $\Delta\langle r^v\rangle_{\mathrm{m}}$ value is not appropriately reproduced.

3 Densities in different pictures

3.1 The four-component Dirac picture

The hydrogenic Dirac orbitals are well known [20, 21]. Since the analytic expressions for the respective densities, $\rho_{\mathrm{e}}(\mathbf{r},\mathbf{s})$, are somewhat clumsy, the radial densities, $P_{\mathrm{e}}(r) = r^2 \int \mathrm{d}\Omega\, \rho_{\mathrm{e}}(\mathbf{r},\mathbf{s})$, are directly plotted for later comparison in Fig. 2. Using four-component Dirac perturbation theory [22–24][1] to first order in α^2 (DPT2), the relativistically pertubed orbitals and densities are derived in unitary normalization (they differ in the latter respect from formulae in the literature [24]):

$$\langle \Psi_i^{\mathrm{D}} | \Psi_j^{\mathrm{D}} \rangle = \delta_{ij} \,,$$
$$\langle \Psi_i^{(0)} | \Psi_j^{(0)} \rangle = \langle \varphi_i^{(0)} | \varphi_j^{(0)} \rangle = \delta_{ij} \,,$$
$$\langle \Psi_i^{(1)} | \Psi_j^{(0)} \rangle + \langle \Psi_i^{(0)} | \Psi_j^{(1)} \rangle = \langle \varphi_i^{(1)} | \varphi_j^{(0)} \rangle + \langle \varphi_i^{(0)} | \varphi_j^{(1)} \rangle + \langle \chi_i^{(0)} | \chi_j^{(0)} \rangle = 0 \,.$$

One obtains for the radial wavefunctions Eqs. (14)–(21). $\tilde{\gamma}$ is the Euler–Mascheroni constant, $\tilde{\gamma} \approx 0.577216$, and $\varphi(r)$ and $\chi(r)$ are the upper and lower components of the orbitals, cf. Eq. (3), after integration over angles. For the respective densities up to first order in α^2, Eq. (5), one obtains Eqs. (22)–(25).

3.2 The two-component Newton–Wigner picture

Since a general analytic expression for U in Eq. (9) is not known except for free electrons, one possible way is to construct the decoupling transformation, U, in a recursive manner. For the previously mentioned choices, namely the Foldy–Wouthuysen and CPD expansions, explicit formulae are obtained (the DKH approach being a numerically available highly accurate intermediate [25]). Transforming the Pauli solutions of Moss et al. [26, 27] to unitary normalization, we obtain $\tilde{\varphi} = \tilde{\varphi}^{(0)} + \alpha^2 \tilde{\varphi}^{(1)}$ with $\tilde{\varphi}^{(0)} = \varphi^{(0)}$ and Eqs. (26)–(29).

[1] Some authors [14, 24] prefer the name "direct" perturbation theory, since the perturbation expansion is performed "directly" with the Dirac operator, not after transformation to two-component pictures

The corresponding densities up to order α^2 are displayed in Eqs. (30)–(33).

The ZORA densities for the standard gauge of the electric potential are obtained from the Dirac functions,

$$\varphi_{1s_{1/2}}(r) = 2Z^{3/2}\mathrm{e}^{-Zr}\left\{1 - \frac{Z^2\alpha^2}{2}\left[\ln(2Zr) + \tilde{\gamma} - 5/4\right]\right\} + \mathcal{O}(\alpha^4) \tag{14}$$

$$\chi_{1s_{1/2}}(r) = Z^{5/2}\mathrm{e}^{-Zr}\left\{1 - \frac{Z^2\alpha^2}{2}\left[\ln(2Zr) + \tilde{\gamma} - 7/4\right]\right\} + \mathcal{O}(\alpha^4) \tag{15}$$

$$\varphi_{2s_{1/2}}(r) = \frac{Z^{3/2}}{2\sqrt{2}}\mathrm{e}^{-\frac{Z}{2}r}\left\{(Zr-2) - \frac{Z^2\alpha^2}{32} \times \left[Zr(2Zr + 16\tilde{\gamma} - 43) + 16(Zr-2)\ln(Zr) - 32\tilde{\gamma} + 46\right]\right\} + \mathcal{O}(\alpha^4) \tag{16}$$

$$\chi_{2s_{1/2}}(r) = \frac{Z^{5/2}}{8\sqrt{2}}\mathrm{e}^{-\frac{Z}{2}r}\left\{(Zr-4) - \frac{Z^2\alpha^2}{32} \times \left[Zr(2Zr + 16\tilde{\gamma} - 53) + 16(Zr-4)\ln(Zr) - 64\tilde{\gamma} + 124\right]\right\} + \mathcal{O}(\alpha^4) \tag{17}$$

$$\varphi_{2p_{1/2}}(r) = \frac{Z^{3/2}}{2\sqrt{6}}\mathrm{e}^{-\frac{Z}{2}r}\left\{Zr - \frac{Z^2\alpha^2}{96} \times \left[Zr(6Zr + 48\tilde{\gamma} - 109) + 48Zr\ln(Zr) - 72\right]\right\} + \mathcal{O}(\alpha^4) \tag{18}$$

$$\chi_{2p_{1/2}}(r) = \frac{Z^{5/2}}{8\sqrt{6}}\mathrm{e}^{-\frac{Z}{2}r}\left\{(Zr-6) - \frac{Z^2\alpha^2}{96} \times \left[Zr(6Zr + 48\tilde{\gamma} - 163) + 48(Zr-6)\ln(Zr) - 288\tilde{\gamma} + 570\right]\right\} + \mathcal{O}(\alpha^4) \tag{19}$$

$$\varphi_{2p_{3/2}}(r) = \frac{Z^{3/2}}{2\sqrt{6}}\mathrm{e}^{-\frac{Z}{2}r}Zr \times \left\{1 - \frac{Z^2\alpha^2}{96}\left[24\ln(Zr) + 24\tilde{\gamma} - 47\right]\right\} + \mathcal{O}(\alpha^4) \tag{20}$$

$$\chi_{2p_{3/2}}(r) = \frac{Z^{5/2}}{8\sqrt{6}}\mathrm{e}^{-\frac{Z}{2}r}Zr \times \left\{1 - \frac{Z^2\alpha^2}{96}\left[24\ln(Zr) + 24\tilde{\gamma} - 53\right]\right\} + \mathcal{O}(\alpha^4) \tag{21}$$

$$\rho^{\mathrm{D}}_{1s_{1/2}}(r) = 4Z^3\mathrm{e}^{-2Zr}\left\{1 - Z^2\alpha^2[\ln(2Zr) + \tilde{\gamma} - 3/2]\right\} + \mathcal{O}(\alpha^4) \tag{22}$$

$$\rho^{\mathrm{D}}_{2s_{1/2}}(r) = \frac{1}{8}Z^3\mathrm{e}^{-Zr}\left((Zr-2)^2 - \frac{Z^2\alpha^2}{8}\left\{(Zr-2)\right.\right.$$
$$\times\left[Zr\left(Zr + 8\tilde{\gamma} - \frac{43}{2}\right) - 16\tilde{\gamma} + 23\right.$$
$$\left.\left.\left. + 8(Zr-2)\ln(Zr)\right] - \frac{(Zr-4)^2}{2}\right\}\right) + \mathcal{O}(\alpha^4) \tag{23}$$

$$\rho^{\mathrm{D}}_{2p_{1/2}}(r) = \frac{1}{24}Z^3\mathrm{e}^{-Zr}\left((Zr)^2 - \frac{Z^2\alpha^2}{24}\right.$$
$$\times\left\{24(Zr)^2\ln(Zr) + Zr\right.$$
$$\left.\left.\times\left[Zr(3Zr + 24\tilde{\gamma} - 56) - 18\right] - 54\right\}\right) + \mathcal{O}(\alpha^4) \tag{24}$$

$$\rho^{\mathrm{D}}_{2p_{3/2}}(r) = \frac{1}{24}Z^3\mathrm{e}^{-Zr}(Zr)^2$$
$$\times\left\{1 - \frac{Z^2\alpha^2}{24}[12\ln(Zr) + 12\tilde{\gamma} - 25]\right\} + \mathcal{O}(\alpha^4) \tag{25}$$

$$\tilde{\varphi}^{(1)}_{1s_{1/2}}(r) = -Z^{3/2}\mathrm{e}^{-Zr}\left(\ln(2Zr) + \tilde{\gamma} - 1 - \frac{1}{2Zr}\right)Z^2 \tag{26}$$

$$\tilde{\varphi}^{(1)}_{2s_{1/2}}(r) = -\frac{Z^{3/2}}{32\sqrt{2}}\mathrm{e}^{-\frac{Zr}{2}} \times \left(Zr(Zr + 8\tilde{\gamma} - 21) + 8(Zr-2)\right.$$
$$\left.\times\ln(Zr) - 16\tilde{\gamma} + 18 + \frac{8}{Zr}\right)Z^2 \tag{27}$$

$$\tilde{\varphi}^{(1)}_{2p_{1/2}}(r) = -\frac{Z^{3/2}}{96\sqrt{6}}\mathrm{e}^{-\frac{Zr}{2}}[Zr(3Zr + 24\tilde{\gamma} - 53)$$
$$+ 24Zr\ln(Zr) - 48]Z^2 \tag{28}$$

$$\tilde{\varphi}^{(1)}_{2p_{3/2}}(r) = -\frac{Z^{3/2}}{48\sqrt{6}}\mathrm{e}^{-\frac{Zr}{2}}$$
$$\times[Zr(6\tilde{\gamma} - 11) + 6Zr\ln(Zr) - 6]Z^2 \tag{29}$$

$$\tilde{\rho}^{\mathrm{P}}_{1s_{1/2}}(r) = 4Z^3\mathrm{e}^{-2Zr}$$
$$\times\left[1 - Z^2\alpha^2\left(\ln(2Zr) + \tilde{\gamma} - 1 - \frac{1}{2Zr}\right)\right] + \mathcal{O}(\alpha^4) \tag{30}$$

$$\tilde{\rho}^{\mathrm{P}}_{2s_{1/2}}(r) = \frac{1}{8}Z^3\mathrm{e}^{-Zr}\left[(Zr-2)^2 - \frac{Z^2\alpha^2}{8}(Zr-2)\right.$$
$$\times\left(Zr(Zr + 8\tilde{\gamma} - 21) - 16\tilde{\gamma} + 18\right.$$
$$\left.\left. + 8(Zr-2)\ln(Zr) + \frac{8}{Zr}\right)\right] + \mathcal{O}(\alpha^4) \tag{31}$$

$$\tilde{\rho}^{\mathrm{P}}_{2p_{1/2}}(r) = \frac{1}{24}Z^3\mathrm{e}^{-Zr}(Zr)^2\left[1 - \frac{Z^2\alpha^2}{24}\left(24\ln(Zr) + 3Zr\right.\right.$$
$$\left.\left. + 24\tilde{\gamma} - 53 - \frac{48}{Zr}\right)\right] + \mathcal{O}(\alpha^4) \tag{32}$$

$$\tilde{\rho}^{\mathrm{P}}_{2p_{3/2}}(r) = \frac{1}{24}Z^3\mathrm{e}^{-Zr}(Zr)^2$$
$$\times\left[1 - \frac{Z^2\alpha^2}{24}\left(12\ln(Zr) + 12\tilde{\gamma} - 22 - \frac{12}{Zr}\right)\right]$$
$$+ \mathcal{O}(\alpha^4) \tag{33}$$

$$\tilde{\rho}^{\mathrm{Z}}_{1s_{1/2}}(r) = 4Z^3\mathrm{e}^{-2Zr}$$
$$\times\left[1 - Z^2\alpha^2\left(\frac{Zr}{2} + \ln(2Zr) + \tilde{\gamma} - \frac{9}{4}\right)\right]$$
$$+ \mathcal{O}(\alpha^4) \tag{34}$$

$$\tilde{\rho}^{\mathrm{Z}}_{2s_{1/2}}(r) = \frac{1}{8}Z^3\mathrm{e}^{-Zr}\left\{(Zr-2)^2 - \frac{Z^2\alpha^2}{8}(Zr-2)\right.$$
$$\times\left[Zr\left(\frac{3}{2}Zr + 8\tilde{\gamma} - \frac{51}{2}\right)\right.$$
$$\left.\left.+8(Zr-2)\ln(Zr) - 16\tilde{\gamma} + 27\right]\right\}$$
$$+ \mathcal{O}(\alpha^4) \tag{35}$$

$$\tilde{\rho}^{\mathrm{Z}}_{2p_{1/2}}(r) = \frac{1}{24}Z^3\mathrm{e}^{-Zr}(Zr)^2\left[1 - \frac{Z^2\alpha^2}{24}\left(24\ln(Zr)\right.\right.$$
$$\left.\left. + \frac{9}{2}Zr + 24\tilde{\gamma} - \frac{127}{2} - \frac{36}{Zr}\right)\right] + \mathcal{O}(\alpha^4) \tag{36}$$

$$\tilde{\rho}^{\mathrm{Z}}_{2p_{3/2}}(r) = \frac{1}{24}Z^3\mathrm{e}^{-Zr}(Zr)^2$$
$$\times\left[1 - \frac{Z^2\alpha^2}{24}\left(12\ln(Zr) + 12\tilde{\gamma} - \frac{65}{2} + \frac{3}{2}Zr\right)\right]$$
$$+ \mathcal{O}(\alpha^4) \tag{37}$$

$\tilde{\rho}^{\mathrm{Z}}(\mathbf{r}') = N\,|\varphi(\mathbf{r}'\lambda)|^2$, with the scale factor $\lambda = 1/(1 + \alpha^2 E^{\mathrm{Dirac}}/2m)$ [19] and N being a normalization factor. Up to order α^2 we obtain Eqs. (34)–(37). The respective $\langle r\rangle$ and $\langle 1/r\rangle$ expectation values are displayed in Table 1.

4 Results and discussion

Relativistic changes of densities [21] are plotted in Fig. 2 as $\Delta^{\mathrm{rel}}P(r) = (r^2/Z^3\alpha^2)[\rho(r) - \rho^{(0)}(r)]$ versus $\log_{10}(Zr)$. Comparison of the Dirac density and its DPT2 approximation illustrates the well-known fact that first-order perturbation theory in α^2 (DPT2) is accurate for small Z ($Z = 1$) or large j, while it yields too small relativistic

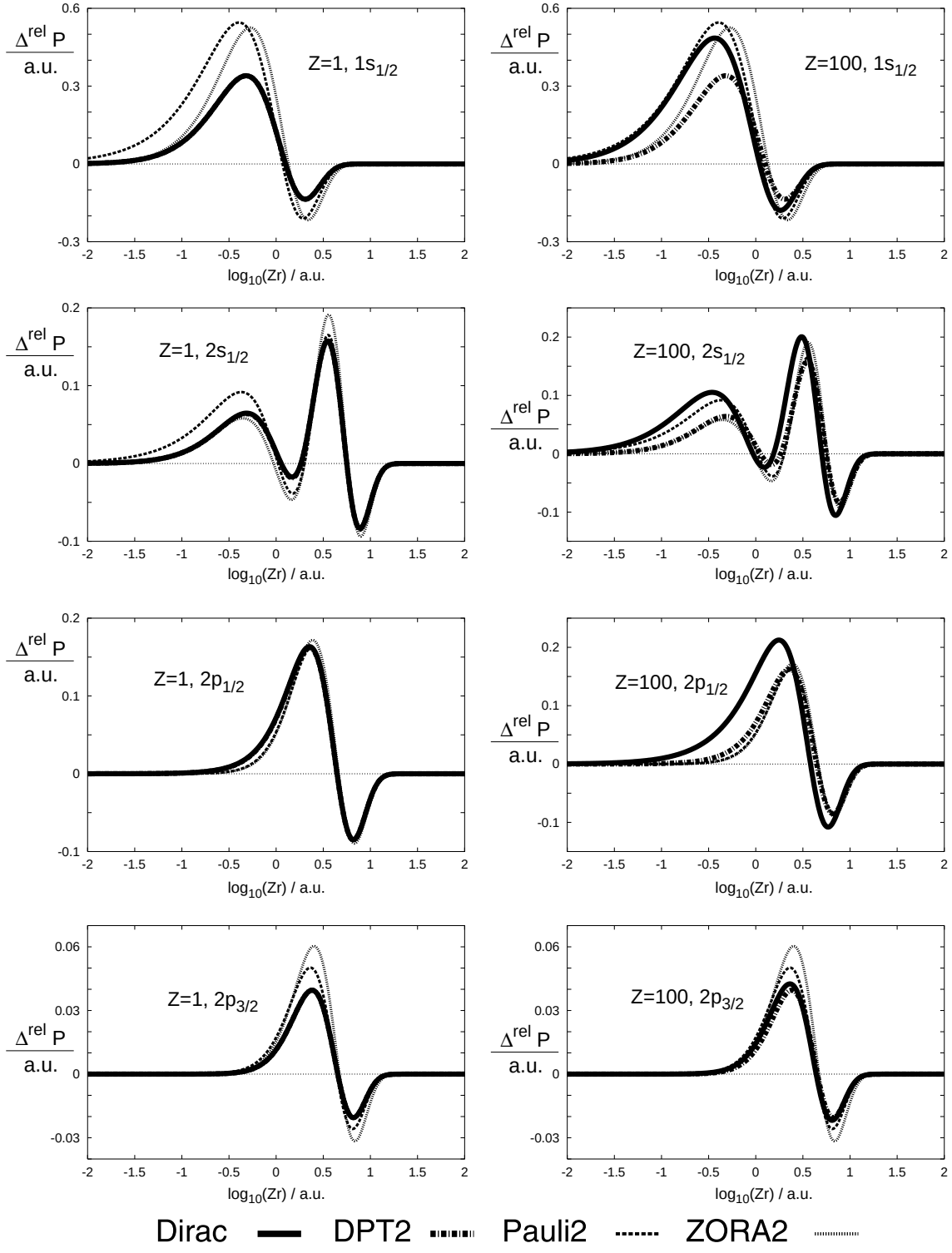

Fig. 2. Relativistic change of radial densities $\Delta^{\mathrm{rel}}P = (r^2/Z^3\alpha^2)\,\Delta^{\mathrm{rel}}\rho(r)$ in different pictures for the four lowest hydrogen-like states of nuclear charges $Z = 1$ and $Z = 100$ versus $\log_{10}(Zr)$ in atomic units. *Dirac*: full relativistic change of the charge density in the Dirac picture; *DPT2*: lowest-order (α^2) change of the charge density; *Pauli2* and *ZORA2*: the respective lowest-order mass density changes as approximations to the Newton–Wigner picture. The same scale is used for r and r'

corrections (here orbital contractions) for large Z ($Z = 100$) and small j ($j = 1/2$).

Concerning the two approximations to the Newton–Wigner density, we remember that the Pauli approximation reproduces the term of $\mathcal{O}(\alpha^2)$ correctly, while ZORA converges better at small r values. Since ZORA yields energies too low, the classical turning point of the state is shifted too strongly inwards and the relativistic

Table 1. Expectation values $\langle r\rangle$ and $\langle 1/r\rangle$ of hydrogen-like orbitals in atomic units for nuclear charge Z. Δ are the relativistic corrections, which correspond to the curves in Figs. 2 and 3 (note the logarithmic abscissa there)

	Level of approximation[a]	Unit	Hydrogenic orbital			
			$1s_{\frac{1}{2}}$	$2s_{\frac{1}{2}}$	$2p_{\frac{1}{2}}$	$2p_{\frac{3}{2}}$
$\langle r\rangle$	Nonrelativistic	$n^2/4Z$	6	6	5	5
$\Delta\langle r\rangle_c$	Dirac2	$nZ\alpha^2/32$	−16	−35	−35	−8
	Dirac ($Z = 92$)		−18.4	−38.8	−38.8	−8.2
$\Delta\langle r\rangle_m$	Pauli2	$nZ\alpha^2/32$	−24	−36	−34	−10
	Newton–Wigner ($Z = 92$)[b]		−24.7	−39.8	−37.7	−10.1
	ZORA2		−28	−38	−37	−13
	ZORA ($Z = 92$)		−29.8	−41.8	−40.6	−13.1
$\langle\frac{1}{r}\rangle$	Nonrelativistic	Z/n^2	1	1	1	1
$\Delta\langle\frac{1}{r}\rangle_c$	Dirac2	$Z^3\alpha^2/24n^3$	12	30	30	6
	Dirac ($Z = 92$)		18.6	47.5	47.5	6.6
$\Delta\langle\frac{1}{r}\rangle_m$	Pauli2	$Z^3\alpha^2/24n^3$	24	42	26	8
	ZORA2		18	27	27	9
	ZORA ($Z = 92$)		29.3	41.4	41.4	9.9

[a] Relativistic corrections in the Dirac charge density (c) picture [Dirac2 is the first-order Dirac pertubation theory in α^2 contribution of $\mathcal{O}(\alpha^2)$] and in the Newton–Wigner mass density (m) picture [Pauli2 is the Pauli approximation of $\mathcal{O}(\alpha^2)$; ZORA is the regular approximation of $\mathcal{O}[E/(2mc^2 - W)$ and ZORA2 the α^2 contribution to it]
[b] Values calculated from Ref. [16]

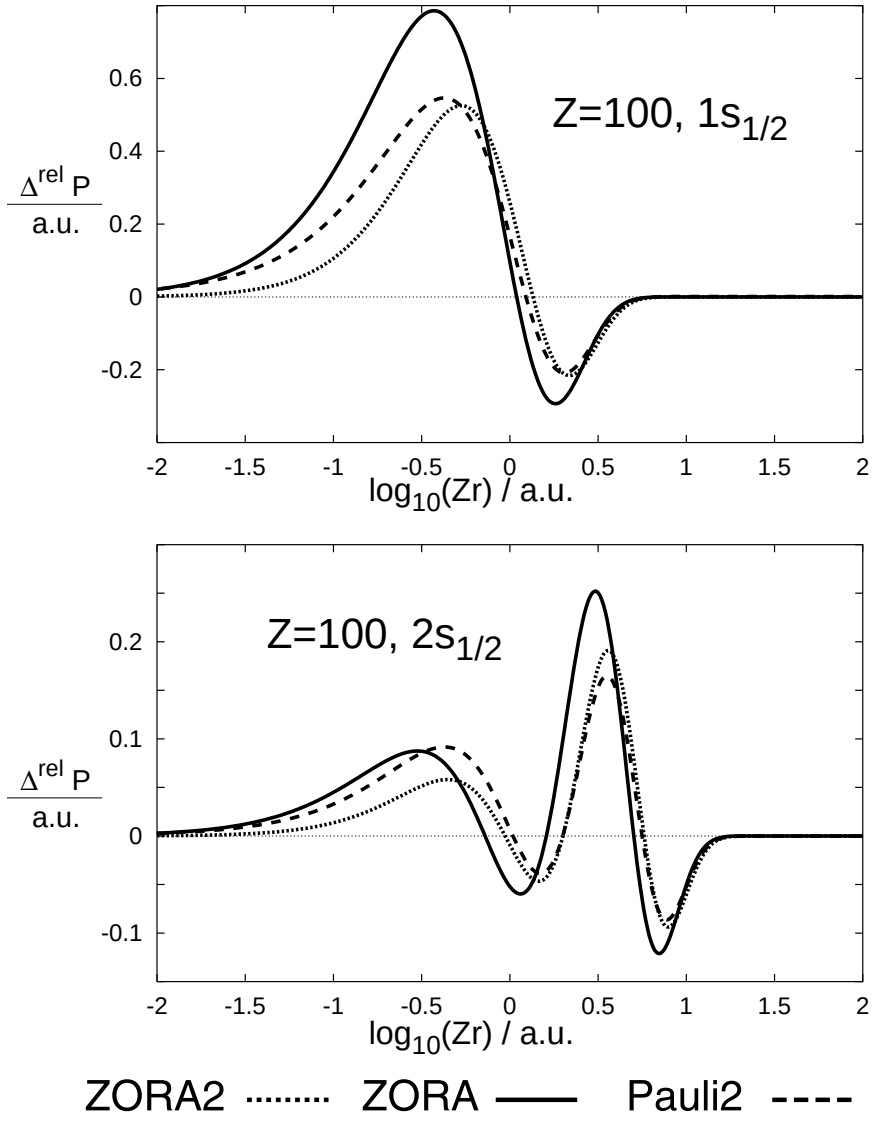

Fig. 3. Relativistic change of radial particle density at the Pauli2, ZORA2 and ZORA levels. See also legend of Fig. 2

contraction of the Newton–Wigner particle density is too large. The opposite holds for the Pauli approximation. Indeed, approaching the nucleus from large r values, the relativistic density contraction (negative ΔP values) in Fig. 2 at the ZORA2 level sets in at larger r values and is bigger than at the Pauli2 level. The relativistic reduction of the $\langle r \rangle$ expectation values is also more pronounced at the ZORA2 than at the Pauli2 level [compare $\Delta\langle r \rangle_{\mathrm{m}}$, Pauli2 with ZORA2 or Newton–Wigner ($Z = 92$) with ZORA ($Z = 92$) in Table 1]. We note that the higher-order effects (the difference between second order and the full contribution for $Z = 92$) are rather similar for the Dirac and the Newton–Wigner and the ZORA values, except concerning the $1s$ state. The exceptional sensitivity of $1s$ to relativistic effects has already been mentioned [16].

Concerning the difference between the Dirac charge position and the Newton–Wigner mass position, it follows from the operator expressions in Table 1 of Ref. [13] (see also Sect. 1.7 of Ref. [4]) that

$$\begin{aligned} \langle r^2 \rangle_{\mathrm{c}} - \langle r^2 \rangle_{\mathrm{m}} &= \langle r^2 \rangle_{\mathrm{Dirac}} - \langle r^2 \rangle_{\mathrm{Newton\text{–}Wigner}} \\ &= \alpha^2 \langle \mathbf{s}\, \mathbf{j} \rangle \end{aligned} \tag{38}$$

with

$$\langle \mathbf{s}\, \mathbf{j} \rangle = \langle \mathbf{s}(\mathbf{l} + \mathbf{s}) \rangle = \langle \mathbf{s}^2 \rangle + \langle \mathbf{l} \cdot \mathbf{s} \rangle = \frac{3}{4} + \frac{\kappa - 1}{2} \quad , \tag{39}$$

which is positive or negative for κ positive ($j = l + 1/2$) or negative ($j = l - 1/2$), respectively [12]. The same relation holds for $\langle r \rangle_{\mathrm{c}} - \langle r \rangle_{\mathrm{m}} = \alpha^2 Z \kappa / 4n^2$ [13] (Table 1). The ZORA level is not accurate enough to reproduce this trend (see the $2p_{1/2}$ values in Table 1).

The situation near the nucleus is more complicated. At the Pauli level the relativistic damping of the potential divergency is not fully accounted for (Fig. 1). Although the relativistic contraction of the Pauli function is too weak in most regions of space, it becomes too large in the vicinity of the nucleus. See the $1/Zr$ terms in Eqs. (30)–(33) which are absent in Eqs. (34), (35), and (37). Compare also the Pauli2 and ZORA2 curves of the $1s$ and $2s$ states for small r values in Fig. 2. On the other hand, the comparison of ZORA2 and ZORA in Fig. 3 shows that higher-order terms of course become especially important in the vicinity of the nucleus. The Pauli2 approximation shows the right trend there.

Concerning the ZORA energies, the largest errors in the relativistic corrections occur for the states of highest κ value for given n: at $\mathcal{O}(\alpha^2)$ $\Delta^{\mathrm{rel}} E^{\mathrm{ZORA}}$ is twice as big as $\Delta^{\mathrm{rel}} E^{\mathrm{Dirac}}$ for $1s_{1/2}$, $2p_{3/2}$, $3d_{5/2}$ etc. [11, 19]. Concerning other expectation values such as $\langle r \rangle$ or $\langle 1/r \rangle$, ZORA, as an approximation of the Foldy–Wouthuysen, i.e. Newton–Wigner, representation, yields qualitatively incorrect relativistic corrections also for other states. The ZORA errors are of the same order of magnitude as the relativistic corrections themselves or at least as the differences between the Dirac and the Newton–Wigner operators also for low κ states such as $2s_{1/2}$ or $2p_{1/2}$. Higher orders of the RA are needed for expectation values, especially for Coulombic $\kappa = n$ states, even for small nuclear charges. Note that the relativistic corrections for given n are in general smallest for $\kappa = n$ and therefore fractional differences and fractional corrections are blown up for $2p_{3/2}$, $3d_{5/2}$, etc. On the other hand, ZORA is known to be rather accurate for valence states in many-electron systems [10, 11], for which the difference of charge and mass position is known to be small anyhow [13].

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