Exact solutions of regular approximate relativistic wave equations for hydrogen-like atoms

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Apart from relativistic effects originating from high kinetic energy of an electron in a flat potential, which are treated in first order by the Pauli Hamiltonian, there are relativistic effects even for low-energy electrons if they move in a strong Coulomb potential. The latter effects can be accurately treated already in the zeroth order of an expansion of the Foldy–Wouthuysen transformation, if the expansion is carefully chosen to be nondivergent for $r \rightarrow 0$ even for Coulomb potentials, as shown by Van Lenthe *et al.* [J. Chem. Phys. **99**, 4597 (1993)] (cf. also Heully *et al.* [J. Phys. B **19**, 2799 (1986)] and Chang *et al.* [Phys. Scr. **34**, 394 (1986)]). In the present paper, it is shown that the solutions of the zeroth order of this two-component regular approximate (ZORA) equation for hydrogen-like atoms are simply scaled solutions of the large component of the Dirac wave function for this problem. The eigenvalues are related in a similar way. As a consequence, it is proven that under some restrictions, the ZORA Hamiltonian is bounded from below for Coulomb-like potentials. Also, an exact result for the first order regular approximate Hamiltonian is given. The method can also be used to obtain exact results for regular approximations of scalar relativistic equations, like the Klein–Gordon equation. The balance between relativistic effects originating from the Coulombic singularity in the potential (typically core penetrating s and p valence electrons in atoms and molecules) and from high kinetic energy (important for high-energy electrons in a flat potential and also for core-avoiding high angular momentum (d, f, and g states in atoms) are discussed.

I. INTRODUCTION

One of the most important problems in quantum mechanics, that can be solved exactly, is the problem of an electron moving in a Coulomb field. The bound-state solutions of the Schrödinger and Klein–Gordon equation for hydrogen-like atoms were already obtained in the early days of quantum mechanics.[1,2] For this system the solutions of the Dirac equation are also known,[3,4] which is very convenient when considering approximations. The Schrödinger equation may be considered to be the zeroth order equation of the expansion in c^{-1} of the exact Foldy–Wouthuysen transformed Dirac equation. A better expansion in the case of a Coulomb-like field is the one derived by Heully *et al.*,[5] Chang *et al.*,[6] and Van Lenthe *et al.*[7] In this paper we will give an exact relation between the Dirac solutions and the solutions of the zeroth order of this regular approximate (ZORA) equation in the case of hydrogen-like atoms. Exact solutions of these one electron systems are very useful as a starting point for the calculations on more complex systems.

The solution of the four-component Dirac equation for more complex systems than a hydrogen atom is very time consuming. Since in most cases one is not interested in the negative energy continuum of the Dirac equation, it would therefore be very attractive to have the exact Foldy–Wouthuysen transformation, which decouples the Dirac equation into a two-component equation for the positive total energies and one for the negative total energies. The conventional way is to do an expansion in c^{-1} of this Foldy–Wouthuysen transformed Dirac Hamiltonian for positive total energies, which gives in zeroth order the nonrelativistic Hamiltonian and in first order the Pauli Hamiltonian. The difference between this approach and the one proposed in Refs. 5–7 is the way the expansion is carried out. To obtain the Schrödinger equation one implicitly or explicitly is expanding in $(E-V)/2c^2$, whereas for the regular approximate equation the expansion is done in $E/(2c^2-V)$.[7] The first expansion is invalid for particles in a Coulomb potential, where there will always be a region of space (close to the nucleus) where $(E-V)/2c^2>1$. The regular approximate expansion remains valid in that region.

We wish to stress that a proper expansion in the immediate neighborhood of the nucleus is important, also for valence electrons. For a long time it has been believed that the low energy of valence electrons would imply that relativistic effects would be very small, e.g., valence ionization energies and chemical bond energies of heavy element compounds. During the 1970's actual calculations, however, demonstrated that relativistic effects are quite significant for these properties. The origin of this large relativistic effect for these low-energy electrons is the Coulombic singularity of the potential, as has been analyzed by Schwarz *et al.*[8] These authors showed that the relativistic effects, also for valence electrons, originate in the immediate neighborhood of the nucleus. Classically this means that the relativistic effects arise when the valence electron is close to the nucleus and has a very large kinetic energy, even if its binding energy (ionization energy or orbital energy) is small. It was noted[8] that the kinetic and potential energy of a valence electron do not have a virial ratio to the one-electron energy but are much larger. It is therefore understandable that an expansion of the transformed two-component Hamiltonian that treats

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the Coulombic singularity properly is crucial. In a recent paper[7] it was shown that such a regular expansion leads to relativistic effects already in zeroth order. The zeroth order regular approximation (ZORA) was successfully used in an all-electron calculation of the uranium atom and was shown to give very accurate results for the valence orbitals. The zeroth order with proper treatment of the Coulomb singularity proves, in fact, much more accurate than the traditional first order Pauli Hamiltonian. This conclusion only holds if the relativistic effects originate from the Coulombic singularity in the potential. In a flat potential the ZORA Hamiltonian reduces to the nonrelativistic Hamiltonian and is therefore not able to describe relativistic effects arising from high kinetic energy of the electrons, such as the mass-velocity correction (see Sec. VII). High angular momentum orbitals, that avoid the nuclear region due to the centrifugal barrier, approach this situation more closely and are therefore not necessarily described more accurately by the zero order regular approximation than by the Pauli approximation. In all cases the first order regular approximation is expected to be superior to the conventional first order (Pauli) approximation.

The present paper investigates first the boundedness from below the ZORA Hamiltonian, and discusses in more detail the balance between the two types of relativistic effects identified above, i.e., the ones originating from the Coulombic singularity and the ones due to high kinetic energy. It was stated in Ref. 7 that the ZORA Hamiltonian—in contrast to the Pauli Hamiltonian—is bounded from below in the case of a Coulomb-like potential. In Sec. III we will prove this statement after obtaining the exact solutions of the ZORA equation for hydrogen-like atoms. It will be shown that the boundedness from below is not true for atoms with point charge $Z>c$ ($c\approx 137.037$ in atomic units). In Sec. IV we will give an exact result for the first order of the regular approximate Hamiltonian in the case of a hydrogen-like atom.

In Sec. V we can use the arguments of the preceding sections to obtain exact results for regular approximations to scalar relativistic equations. These approximations to a scalar relativistic equation from Refs. 9 and 10 and the Klein–Gordon equation again are obtained by an expansion in $E/(2c^2-V)$ of these equations.

In Sec. VII we will compare the solutions of the different equations in the case of the one-electron system uranium 91+, where both a strong Coulomb potential is present and the electron energy is high.

We finally note that we have chosen in this paper the natural gauge in which the potential tends to zero at infinity, $V(\mathbf{r})\to 0$ for $|\mathbf{r}|\to\infty$. This point is not completely trivial since the ZORA Hamiltonian is not gauge-invariant in the sense that adding a constant to $V(\mathbf{r})$ does not change the eigenvalue by exactly the same constant. This question will be dealt with in detail, in connection with the calculation of ionization energies and molecular bond energies, in a subsequent paper.

II. EXACT SOLUTIONS FOR HYDROGEN-LIKE ATOMS

We are looking for hydrogen-like solutions of the zeroth order regular approximate (ZORA) equation, which is given in atomic units by

$$\tilde{H}_0\tilde{\Phi}_0\equiv\left(V+\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{2c^2-V}\,\boldsymbol{\sigma}\cdot\mathbf{p}\right)\tilde{\Phi}_0=\tilde{E}_0\tilde{\Phi}_0 \tag{1}$$

where

$$V=-\frac{Z}{r} \tag{2}$$

is the Coulomb potential of a point charge Z. The ZORA eigenfunctions $\tilde{\Phi}_0$ belonging to different eigenvalues $\tilde{E}_0$ are orthogonal, because the ZORA Hamiltonian $\tilde{H}_0$ is energy-independent and Hermitian. We can relate the solutions of the ZORA equation to the well known solutions of the Dirac equation for this problem. After elimination of the small component the equation for the large component ϕ^D of the four-component Dirac spinor is

$$\left(-\frac{Z}{r}+\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{2c^2+E^D+\dfrac{Z}{r}}\,\boldsymbol{\sigma}\cdot\mathbf{p}\right)\phi^D(\mathbf{r})=E^D\phi^D(\mathbf{r}). \tag{3}$$

We can transform this equation to the ZORA equation by means of an energy-dependent scaling with λ of the coordinate $\mathbf{r}$

$$\mathbf{r}'=\lambda\mathbf{r}, \tag{4}$$

hence

$$\boldsymbol{\sigma}\cdot\mathbf{p}'=\frac{1}{\lambda}\,\boldsymbol{\sigma}\cdot\mathbf{p}. \tag{5}$$

After dividing by λ, this transforms Eq. (3) into

$$\left(-\frac{Z}{r'}+\boldsymbol{\sigma}\cdot\mathbf{p}'\,\frac{c^2}{\dfrac{2c^2+E^D}{\lambda}+\dfrac{Z}{r'}}\,\boldsymbol{\sigma}\cdot\mathbf{p}'\right)\phi^D\left(\frac{\mathbf{r}'}{\lambda}\right)=\frac{E^D}{\lambda}\,\phi^D\left(\frac{\mathbf{r}'}{\lambda}\right). \tag{6}$$

Defining the energy-dependent λ by

$$\lambda=\frac{2c^2+E^D}{2c^2} \tag{7}$$

one obtains

$$\left(-\frac{Z}{r'}+\boldsymbol{\sigma}\cdot\mathbf{p}'\,\frac{c^2}{2c^2+\dfrac{Z}{r'}}\,\boldsymbol{\sigma}\cdot\mathbf{p}'\right)\phi^D\left(\frac{\mathbf{r}'}{\lambda}\right)=\frac{2c^2E^D}{2c^2+E^D}\,\phi^D\left(\frac{\mathbf{r}'}{\lambda}\right). \tag{8}$$

Here one recognizes the one-particle ZORA equation (1). Thus, for every solution of the Dirac equation with energy E^D, we find a solution of the ZORA equation with energy $\tilde{E}_0$

$$\tilde{E}_0=\frac{2c^2E^D}{2c^2+E^D} \tag{9}$$

with corresponding eigenfunction $\tilde{\Phi}_0$

$$\tilde{\Phi}_0(\mathbf{r}) = \phi^D\left(\frac{\mathbf{r}}{\lambda}\right). \tag{10}$$

Thus, the ZORA eigenfunctions are scaled Dirac large components, in which the scaling factor depends on the energy. The number of nodes in the ZORA eigenfunction is the same as in the large component of the Dirac spinor, because only a scaling has been applied. The derivation of the relativistic virial theorem[11] was also done by scaling of coordinates. From this theorem we can conclude, that the norm of the Dirac large component, belonging to the discrete spectrum in the case of a hydrogen-like atom, is related to its eigenvalue as

$$\langle \phi^D | \phi^D \rangle = \frac{2c^2 + E^D}{2c^2}. \tag{11}$$

This norm is the same as the energy-dependent λ we used to scale the Dirac equation.

III. BOUNDEDNESS FROM BELOW OF THE ZORA HAMILTONIAN

After finding the exact relation between the eigenvalues of the Dirac and the zeroth order regular approximate (ZORA) Hamiltonian in the case of a hydrogen-like atom, we are now in a position to answer the important question, whether the ZORA Hamiltonian is bounded from below. From Eq. (9) we know that the relation between the eigenvalues is

$$\tilde{E}_0 = \frac{2c^2 E^D}{2c^2 + E^D}. \tag{12}$$

For $Z<c$ the Dirac equation has eigenvalues below $-2c^2$ (negative energy continuum), between $-c^2$ and 0 (discrete spectrum), and above zero (positive energy continuum). According to Eq. (12) these parts of the Dirac spectrum are mapped onto the ZORA spectrum as follows (see Fig. 1): the positive energy continuum $(0,\infty)$ onto $(0,2c^2)$; the discrete part $(-c^2,0)$ onto $(-2c^2,0)$; the negative energy continuum $(-\infty,-2c^2)$ onto $(2c^2,\infty)$. So all the eigenvalues of the ZORA equation are larger than $-2c^2$, which means that for this potential the zeroth order regular approximate Hamiltonian is bounded from below.

Now suppose the potential is given by

$$V = -\frac{Z}{r} + V_1(r), \tag{13}$$

where V_1 is larger than zero everywhere. This V_1 will usually be the mean repulsive potential of some electron density. We can divide the ZORA Hamiltonian for this potential in operators, which are all bounded from below

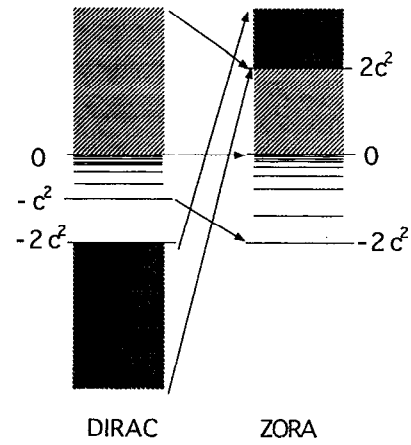

FIG. 1. Relation between Dirac and ZORA eigenvalues for a hydrogen-like atom.

$$\tilde{H}_0 = -\frac{Z}{r} + V_1 + \boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{2c^2 + \frac{Z}{r} - V_1}\,\boldsymbol{\sigma}\cdot\mathbf{p}$$

$$= -\frac{Z}{r} + \boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{2c^2 + \frac{Z}{r}}\,\boldsymbol{\sigma}\cdot\mathbf{p} + V_1$$

$$+ \boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2 V_1}{\left(2c^2 + \frac{Z}{r}\right)\left(2c^2 + \frac{Z}{r} - V_1\right)}\,\boldsymbol{\sigma}\cdot\mathbf{p}. \tag{14}$$

From the discussion at the beginning of this section we know that the first two terms together give an operator that is bounded from below. The last two terms are both positive operators because V_1 is positive and the last operator can be written as the product of an operator with its Hermitian adjoint if $(2c^2 + Z/r - V_1) > 0$. This last condition will always be satisfied in atomic and molecular electronic structure calculations. Note that $V < 2c^2$ implies that the ZORA "kinetic energy" operator $\tilde{T}_0$

$$\tilde{T}_0 = \boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{2c^2 - V}\,\boldsymbol{\sigma}\cdot\mathbf{p} \tag{15}$$

is a positive operator.

The former analysis can be extended to molecular systems, by splitting up the space into regions which contain only one nucleus. In each region the contribution to the expectation value of the Hamiltonian for every wave function is bounded from below (as long as all nuclear charges are smaller than c), since the contributions to the potential coming from the tails of the nuclear potentials of other regions are finite. Consequently, the total Hamiltonian is also bounded from below.

The ZORA Hamiltonian is not bounded from below for a hydrogen-like potential of a point charge with $Z>c$. The Dirac equation then also becomes problematic. To prove that the ZORA Hamiltonian is not bounded from below, we may use the fact that all expectation values of a bounded operator

with some normalized wave function should be larger than a minimum. If we can prove that for some trial wave function the expectation value of this operator can be as negative as one likes, then this operator is not bounded from below. Let us therefore try a wave function Φ^T, with quantum number $\kappa=-1$ and a radial behavior as

$$\Phi^T = r^\alpha\, e^{-\beta r}. \tag{16}$$

Here α should be larger than -1 for the expectation value of the potential to be meaningful. The expectation value $\langle E\rangle$ of the ZORA Hamiltonian is

$$\begin{aligned}\langle E\rangle &= \frac{\langle\Phi^T|\tilde{H}_0|\Phi^T\rangle}{\langle\Phi^T|\Phi^T\rangle} \\ &= \frac{\langle\Phi^T|-\dfrac{Z}{r}+\boldsymbol{\sigma}\cdot\mathbf{p}\,\dfrac{c^2}{2c^2+\dfrac{Z}{r}}\boldsymbol{\sigma}\cdot\mathbf{p}|\Phi^T\rangle}{\langle\Phi^T|\Phi^T\rangle} \\ &< \frac{\langle\Phi^T|-\dfrac{Z}{r}+\boldsymbol{\sigma}\cdot\mathbf{p}\,\dfrac{c^2 r}{Z}\boldsymbol{\sigma}\cdot\mathbf{p}|\Phi^T\rangle}{\langle\Phi^T|\Phi^T\rangle}.\end{aligned} \tag{17}$$

This last term can easily be calculated giving

$$\langle E\rangle < -\frac{Z\beta}{\alpha+1}+\frac{c^2\beta(\alpha+3)}{2Z(\alpha+1)}. \tag{18}$$

Suppose $\alpha=-1+\epsilon$, where ϵ is some small positive number, we can rewrite this as

$$\langle E\rangle < \frac{\beta}{\epsilon}\left(-Z+\frac{c^2(2+\epsilon)}{2Z}\right). \tag{19}$$

Here it can easily be seen that if $Z>c$ we can choose ϵ sufficiently small, so that the term between brackets is negative. Now we still have the freedom to choose β in such a way as to make the term on the right hand side of the inequality as negative as one likes. This proves that the operator is unbounded from below.

If we take the more physical point of view that the nucleus is finite, then the nuclear potential will not have a singularity. The ZORA Hamiltonian in this case is bounded from below if $V < 2c^2$ everywhere, because the potential is bounded from below and the ZORA kinetic energy operator $\tilde{T}_0$ is a positive operator.

IV. FIRST ORDER PERTURBATION

Having obtained the exact zeroth order result for the case of hydrogen-like atoms, we will now obtain an exact result for the first order. We can invert Eq. (9) to

$$E^D = \frac{2c^2\tilde{E}_0}{2c^2-\tilde{E}_0}. \tag{20}$$

Expanding this in powers of c^{-2} gives

$$E^D = \tilde{E}_0+\frac{(\tilde{E}_0)^2}{2c^2}+\cdots. \tag{21}$$

In this section we will see that the regular approximation to first order leads to just this second term in the case of a hydrogen-like atom. The first order regularly approximated (FORA) Hamiltonian $\tilde{H}^{\mathrm{D}}_{\mathrm{FO}}$ is

$$\tilde{H}^D_{\mathrm{FO}} = \tilde{H}_0+\tilde{H}^D_1, \tag{22}$$

where $\tilde{H}^D_1$ is given by

$$\begin{aligned}\tilde{H}^D_1 = &-\frac{1}{2}\,\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{(2c^2-V)^2}\,\boldsymbol{\sigma}\cdot\mathbf{p}\tilde{H}_0 \\ &-\frac{1}{2}\,\tilde{H}_0\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{(2c^2-V)^2}\,\boldsymbol{\sigma}\cdot\mathbf{p}.\end{aligned} \tag{23}$$

The ZORA energy $\tilde{E}_0$ is given by

$$\tilde{E}_0 = \langle\tilde{\Phi}_0|\tilde{H}_0|\tilde{\Phi}_0\rangle. \tag{24}$$

The first order energy is given by the expectation value of the first order Hamiltonian with the zeroth order wave function, thus

$$\begin{aligned}\tilde{E}^D_1 &= \langle\tilde{\Phi}_0|\tilde{H}^D_1|\tilde{\Phi}_0\rangle \\ &= -\tilde{E}_0\langle\tilde{\Phi}_0|\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{\left(2c^2+\dfrac{Z}{r}\right)^2}\,\boldsymbol{\sigma}\cdot\mathbf{p}|\tilde{\Phi}_0\rangle.\end{aligned} \tag{25}$$

In this equation we used that $V=-Z/r$ and that $\tilde{\Phi}_0$ is an eigenfunction of the zeroth order regular approximate (ZORA) Hamiltonian, with eigenvalue $\tilde{E}_0$. We will now prove the following exact relation:

$$\tilde{E}^D_1 = \frac{(\tilde{E}_0)^2}{2c^2} \tag{26}$$

in the case of a hydrogen-like atom. We define a scaled eigenfunction of the ZORA Hamiltonian by

$$\Phi_\lambda(\mathbf{r}) = \lambda^{3/2}\tilde{\Phi}_0(\lambda\mathbf{r}). \tag{27}$$

Because of the prefactor $\lambda^{3/2}$ the scaled wave function is also normalized. We can define the following energy E_λ:

$$E_\lambda = \langle\Phi_\lambda|\tilde{H}_0|\Phi_\lambda\rangle. \tag{28}$$

Because $\tilde{\Phi}_0$ is an eigenvector of the discrete spectrum of $\tilde{H}_0$, its eigenvalue $\tilde{E}_0$ is a stationary value of the functional E_λ,[12] thus

$$\left.\frac{dE_\lambda}{d\lambda}\right|_{\lambda=1} = 0. \tag{29}$$

We can write

$$\begin{aligned}E_\lambda = &\int \lambda^3\tilde{\Phi}^{D\dagger}_0(\lambda\mathbf{r})\frac{-Z}{r}\,\tilde{\Phi}_0(\lambda\mathbf{r})d\mathbf{r} \\ &+\left[\int \lambda^3\tilde{\Phi}^{D\dagger}_0(\lambda\mathbf{r})\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{2c^2+\dfrac{Z}{r}}\,\boldsymbol{\sigma}\cdot\mathbf{p}\tilde{\Phi}_0(\lambda\mathbf{r})d\mathbf{r}\right] \\ &= \lambda\int \tilde{\Phi}^{D\dagger}_0(\lambda\mathbf{r})\frac{-Z}{\lambda r}\,\tilde{\Phi}_0(\lambda\mathbf{r})d(\lambda\mathbf{r})\end{aligned}$$

$$+\left[\lambda^2\int\tilde{\Phi}_0^{D\dagger}(\lambda\mathbf{r})\boldsymbol{\sigma}\cdot\mathbf{p}_\lambda\frac{c^2}{2c^2+\frac{Z\lambda}{\lambda r}}\boldsymbol{\sigma}\cdot\mathbf{p}_\lambda\tilde{\Phi}_0(\lambda\mathbf{r})d(\lambda\mathbf{r})\right]$$

$$=\lambda\langle\tilde{\Phi}_0|\frac{-Z}{r}|\tilde{\Phi}_0\rangle+\lambda\langle\tilde{\Phi}_0|\boldsymbol{\sigma}\cdot\mathbf{p}\frac{c^2}{\frac{2c^2}{\lambda}+\frac{Z}{r}}\boldsymbol{\sigma}\cdot\mathbf{p}|\tilde{\Phi}_0\rangle, \tag{30}$$

where $\boldsymbol{\sigma}\cdot\mathbf{p}_\lambda=(1/\lambda)\boldsymbol{\sigma}\cdot\mathbf{p}$. Now we can use Eq. (29), which gives

$$0=\left.\frac{dE_\lambda}{d\lambda}\right|_{\lambda=1}=\langle\tilde{\Phi}_0|\frac{-Z}{r}|\tilde{\Phi}_0\rangle+\langle\tilde{\Phi}_0|\boldsymbol{\sigma}\cdot\mathbf{p}\frac{c^2}{2c^2+\frac{Z}{r}}\boldsymbol{\sigma}\cdot\mathbf{p}|\tilde{\Phi}_0\rangle$$

$$+2c^2\langle\tilde{\Phi}_0|\boldsymbol{\sigma}\cdot\mathbf{p}\frac{c^2}{\left(2c^2+\frac{Z}{r}\right)^2}\boldsymbol{\sigma}\cdot\mathbf{p}|\tilde{\Phi}_0\rangle$$

$$=\langle\tilde{\Phi}_0|\tilde{H}_0|\tilde{\Phi}_0\rangle-2c^2\frac{\tilde{E}_1^D}{\tilde{E}_0}=\tilde{E}_0-2c^2\frac{\tilde{E}_1^D}{\tilde{E}_0}. \tag{31}$$

Thus,

$$\tilde{E}_1^D=\frac{(\tilde{E}_0)^2}{2c^2}. \tag{32}$$

V. SCALAR RELATIVISTIC EQUATIONS

In quantum chemistry there are many situations where the spin–orbit splitting is not important. One can therefore be interested in a scalar relativistic equation, which has the same symmetry as the Schrödinger equation. In Refs. 9 and 10 such a scalar relativistic equation (SR) was suggested and applied to some atomic and solid state problems. This equation is given by

$$\left(V+\mathbf{p}\frac{c^2}{2c^2+E^{\mathrm{SR}}-V}\mathbf{p}\right)\phi^{\mathrm{SR}}=E^{\mathrm{SR}}\phi^{\mathrm{SR}}. \tag{33}$$

For s orbits, as they are not affected by spin–orbit splitting, the energies that are solutions to this equation are just equal to the eigenvalues of the Dirac equation. The eigenvalues of the orbits with a nonzero angular momentum quantum number are an average of the spin–orbit split eigenvalues of the Dirac equation.[9,10] The zeroth order regular approximate (ZORA) scalar relativistic equation is obtained as the zeroth order term in an expansion in $E/(2c^2-V)$ of this equation

$$\tilde{H}_0^{\mathrm{SR}}\tilde{\Phi}_0^{\mathrm{SR}}\equiv\left(V+\mathbf{p}\frac{c^2}{2c^2-V}\mathbf{p}\right)\tilde{\Phi}_0^{\mathrm{SR}}=\tilde{E}_0^{\mathrm{SR}}\tilde{\Phi}_0^{\mathrm{SR}}, \tag{34}$$

which is just the ZORA Hamiltonian [see Eq. (1)] without spin–orbit coupling. The analytical solutions to this equation for the case of a Coulombic potential can be found for s orbits. For orbitals with a nonzero angular momentum we were not able to find the analytical solutions. However, we were able to find a lower bound to these eigenvalues in terms of the exactly known eigenvalues of the Klein–Gordon equation which will be treated in the next section.

The first order regular approximate (FORA) scalar relativistic Hamiltonian is given by

$$\tilde{H}_{\mathrm{FO}}^{\mathrm{SR}}=\tilde{H}_0^{\mathrm{SR}}+\tilde{H}_1^{\mathrm{SR}}, \tag{35}$$

where

$$\tilde{H}_1^{\mathrm{SR}}=-\frac{1}{2}\mathbf{p}\frac{c^2}{(2c^2-V)^2}\mathbf{p}\tilde{H}_0^{\mathrm{SR}}-\frac{1}{2}\tilde{H}_0^{\mathrm{SR}}\mathbf{p}\frac{c^2}{(2c^2-V)^2}\mathbf{p}. \tag{36}$$

In the case of a hydrogen-like atom all scaling arguments of Secs. II and IV can be repeated, giving the following relations between the eigenvalues and eigenfunctions of the SR and ZORA SR equation

$$\tilde{\Phi}_0^{\mathrm{SR}}(\mathbf{r})=\phi^{\mathrm{SR}}\left(\frac{\mathbf{r}}{\lambda}\right),$$

$$\lambda=\frac{2c^2+E^{\mathrm{SR}}}{2c^2},\quad \tilde{E}_0^{\mathrm{SR}}=\frac{2c^2E^{\mathrm{SR}}}{2c^2+E^{\mathrm{SR}}}, \tag{37}$$

$$\tilde{E}_1^{\mathrm{SR}}=\langle\tilde{\Phi}_0^{\mathrm{SR}}|\tilde{H}_1^{\mathrm{SR}}|\tilde{\Phi}_0^{\mathrm{SR}}\rangle=\frac{(\tilde{E}_0^{\mathrm{SR}})^2}{2c^2}.$$

For s orbitals the ZORA SR equation is the same as the ZORA equation (1). For other orbitals we can write the radial part $\tilde{h}_0^{\mathrm{SR}}$ of the ZORA scalar relativistic operator for a given l as the sum of two radial operators, that are bounded from below (see Sec. III)

$$\tilde{h}_0^{\mathrm{SR}}=\frac{l}{2l+1}\tilde{h}_{0\,(j=l-1/2)}+\frac{l+1}{2l+1}\tilde{h}_{0\,(j=l+1/2)}, \tag{38}$$

where $\tilde{h}_0$ is the radial part of the ZORA Hamiltonian. Because $l>0$ it follows that also $\tilde{H}_0^{\mathrm{SR}}$ is bounded from below.

VI. KLEIN–GORDON EQUATION

In this section we will consider the Klein–Gordon equation. We have two reasons for studying this equation. First of all it is well known that the Klein–Gordon equation, just like the Dirac equation, exhibits a negative continuous eigenvalue spectrum. One might therefore wonder if one could transform the Klein–Gordon equation by the same scaling transformation as used for the Dirac equation, into a Hermitian Hamiltonian equation with an eigenvalue spectrum that is bounded from below. We will show that this is indeed the case. Second, there are some close relations between the Klein–Gordon equation and the scalar relativistic equation considered in the previous section which makes it possible to give a lower bound to eigenvalues of the ZORA SR equation. We will discuss this point further in Sec. VII.

The Klein–Gordon (KG) equation for a particle in a potential V is

$$(E^{\mathrm{KG}}+c^2-V)^2\Psi^{\mathrm{KG}}=(p^2c^2+c^4)\Psi^{\mathrm{KG}}, \tag{39}$$

where E^{KG} is the energy without rest mass. We can rewrite this equation as

$$\left(V+\frac{c^2}{2c^2+E^{\mathrm{KG}}-V}p^2\right)\Psi^{\mathrm{KG}}=E^{\mathrm{KG}}\Psi^{\mathrm{KG}}. \tag{40}$$

An expansion in $E/(2c^2-V)$ in zeroth order gives the regular approximate form of this equation

$$\left(V+\frac{c^2}{2c^2-V}\,p^2\right)\tilde{\Phi}_0^{\mathrm{KG}}=\tilde{E}_0^{\mathrm{KG}}\tilde{\Phi}_0^{\mathrm{KG}}. \tag{41}$$

To make this equation Hermitian, we just have to multiply the Φ's with a weight function

$$\tilde{\Psi}_0^{\mathrm{KG}}=\frac{\sqrt{2c^2-V}}{c}\,\tilde{\Phi}_0^{\mathrm{KG}}. \tag{42}$$

The eigenvalue equation for these functions is Hermitian and this will be called the zeroth order regular approximate (ZORA) Klein–Gordon equation

$$\begin{aligned}\tilde{H}_0^{\mathrm{KG}}\tilde{\Psi}_0^{\mathrm{KG}}&\equiv\left(V+\frac{c}{\sqrt{2c^2-V}}\,p^2\,\frac{c}{\sqrt{2c^2-V}}\right)\tilde{\Psi}_0^{\mathrm{KG}}\\&=\tilde{E}_0^{\mathrm{KG}}\tilde{\Psi}_0^{\mathrm{KG}}.\end{aligned} \tag{43}$$

This equation has the same eigenvalues as Eq. (41). In contrast to the eigenfunctions of Eq. (40) the eigenfunctions of the above Eq. (43) are orthogonal. The first order regular approximate (FORA) Klein–Gordon Hamiltonian $\tilde{H}_{\mathrm{FO}}^{\mathrm{KG}}$ is given by

$$\tilde{H}_{\mathrm{FO}}^{\mathrm{KG}}=\tilde{H}_0^{\mathrm{KG}}+\tilde{H}_1^{\mathrm{KG}}, \tag{44}$$

where

$$\begin{aligned}\tilde{H}_1^{\mathrm{KG}}=&-\frac{1}{2}\,\frac{c}{(2c^2-V)^{3/2}}\,p^2\frac{c}{(2c^2-V)^{1/2}}\;\tilde{H}_0^{\mathrm{KG}}\\&-\frac{1}{2}\,\tilde{H}_0^{\mathrm{KG}}\,\frac{c}{(2c^2-V)^{1/2}}\,p^2\frac{c}{(2c^2-V)^{3/2}}.\end{aligned} \tag{45}$$

The first order energy is given by

$$\tilde{E}_1^{\mathrm{KG}}=\langle\tilde{\Psi}_0^{\mathrm{KG}}|\tilde{H}_1^{\mathrm{KG}}|\tilde{\Psi}_0^{\mathrm{KG}}\rangle=\langle\tilde{\Phi}_0^{\mathrm{KG}}|\frac{-\tilde{E}_0^{\mathrm{KG}}c^2}{(2c^2-V)^2}\,p^2|\tilde{\Phi}_0^{\mathrm{KG}}\rangle. \tag{46}$$

In the case of a hydrogen-like atom $V=-Z/r$ we can follow the same path as in Sec. II to find that the eigenvalues and eigenfunctions of Eq. (41) are scaled eigenvalues and eigenfunctions of Eq. (40)

$$\begin{aligned}&\tilde{\Phi}_0^{\mathrm{KG}}(\mathbf{r})=\frac{c}{\sqrt{2c^2+\frac{Z}{r}}}\,\tilde{\Psi}_0^{\mathrm{KG}}(\mathbf{r})=\Psi^{\mathrm{KG}}\left(\frac{\mathbf{r}}{\lambda}\right),\\&\lambda=\frac{2c^2+E^{\mathrm{KG}}}{2c^2},\quad \tilde{E}_0^{\mathrm{KG}}=\frac{2c^2E^{\mathrm{KG}}}{2c^2+E^{\mathrm{KG}}}.\end{aligned} \tag{47}$$

Following the arguments of Sec. IV we find an expression for the first order energy

$$\tilde{E}_1^{\mathrm{KG}}=\frac{(\tilde{E}_0^{\mathrm{KG}})^2}{2c^2}. \tag{48}$$

The solutions of the Klein–Gordon equation are well known. For $Z<c/2$ the Klein–Gordon equation has eigenvalues below $-2c^2$ (negative energy continuum), between $(1/\sqrt{2}-1)c^2$ and 0 (discrete spectrum), and above zero (positive energy continuum). Now we can use Eq. (47) and the arguments of Sec. III to prove that the ZORA KG Hamiltonian is bounded from below for a Coulomb-like potential with $Z<c/2$.

Analogous to Ref. 7 we can define a family of zeroth order extended Klein–Gordon Hamiltonians $H_0^{\mathrm{ext\ KG}}$

$$\begin{aligned}&H_0^{\mathrm{ext\ KG}}\Psi_0^{\mathrm{ext\ KG}}\\&=\left(V\left(\frac{2c^2-V}{2c^2-\zeta V}\right)+\frac{c}{\sqrt{2c^2-\zeta V}}\,p^2\frac{c}{\sqrt{2c^2-\zeta V}}\right)\Psi_0^{\mathrm{ext\ KG}}.\end{aligned} \tag{49}$$

If $\zeta=2$ then we obtain the extended form[7] of the scalar relativistic ZORA KG equation. This equation can be solved exactly for the hydrogen-like atom for arbitrary ζ and is then closely related to the former ones by some simple subtitutions. If one requires the difference in the eigenvalues of this equation and of the Klein–Gordon equation to be of order c^{-4}, the value $\zeta=\frac{3}{2}$ is obtained. If one compares the eigenvalues of Eq. (49) with the exact Klein–Gordon ones, they are indeed most accurate for this value of ζ (see Sec. VII).

VII. RESULTS

In this section we will first use the exact results for hydrogenic systems obtained in this paper to give a more complete assessment of the performance of the regular approximation. In Ref. 7 it has been extensively documented that for the low-energy valence electrons in a many-electron atom such as U, already the ZORA results yield excellent agreement with Dirac calculations. The error of the ZORA eigenvalues was estimated to be approximately $-E^2/2c^2$, which is corroborated by the result of Sec. IV [see Eq. (26)]. This implies that the error is quite small for low energy valence electrons. The error may, however, become large for high energies. In order to understand the different ways the regular approximation and the conventional Pauli approximation treat relativistic effects for low and high energy electrons, it is useful to distinguish the following cases:

(a) The energy is large, but the potential is small in comparison.

Consequently, we have large momentum everywhere. This situation arises, for example, for a free electron moving at relativistic velocities. In this case the ZORA Hamiltonian reduces to the nonrelativistic Hamiltonian

$$\tilde{H}_0=\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{2c^2-V}\,\boldsymbol{\sigma}\cdot\mathbf{p}=\frac{p^2}{2}. \tag{50}$$

Obviously, the ZORA Hamiltonian does not contain any relativity at all in this case and in particular the mass-velocity correction is entirely absent. In this case the Pauli approximation is clearly superior to the zeroth order regular approximation. The first order regular approximation is needed in this case to introduce the Pauli type corrections

$$\tilde{H}_1=-\frac{1}{2}\,H_0\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{(2c^2-V)^2}\,\boldsymbol{\sigma}\cdot\mathbf{p}+\mathrm{c.c.}\approx-\frac{p^4}{8c^2}. \tag{51}$$

Of course, if $V=0$ the traditional expansion in $(E-V)/2c^2$ is identical to the regular expansion in $E/(2c^2-V)$ and the NR and Pauli Hamiltonians are identical to the ZORA and FORA Hamiltonians.

(b) The energy is small, but there are regions of high potential.

This is the situation for the valence electrons of heavy elements. Classically speaking the momentum is only large in those regions where the potential is large as well. In this case the ZORA Hamiltonian does recover the bulk of the relativistic effects. It in fact does include in this case the mass-velocity corrections as can be seen by reexpanding the ZORA Hamiltonian in inverse powers of c

$$\tilde{H}_0=\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{2c^2-V}\,\boldsymbol{\sigma}\cdot\mathbf{p}\approx\frac{p^2}{2}+\frac{1}{4c^2}\,\boldsymbol{\sigma}\cdot\mathbf{p}V\boldsymbol{\sigma}\cdot\mathbf{p}$$

$$\approx\frac{p^2}{2}+\frac{1}{4c^2}\,\boldsymbol{\sigma}\cdot\mathbf{p}(V-E)\boldsymbol{\sigma}\cdot\mathbf{p}+E\frac{p^2}{4c^2}$$

$$\approx\frac{p^2}{2}-\frac{p^4}{8c^2}+E\,\frac{p^2}{4c^2}\,. \tag{52}$$

However, in the case of the singular Coulomb potential we have seen that this expansion is not really justified and, in fact, the ZORA Hamiltonian sums the increasingly divergent terms in the Pauli expansion to infinite order leading to a final result that is entirely regular. Therefore, in this case even the ZORA Hamiltonian is far superior to the Pauli Hamiltonian. This point has been extensively discussed in Ref. 7.

(c) The energy is high and there is a strong (Coulombic) potential.

In this case the last term in Eq. (52) becomes important. We note in passing that a high and positive E corresponding to an unbound electron would bring about the case (a) effects: the last term would cancel the second (mass-velocity) term in $\tilde{H}_0$. We focus on the interesting case of a bound electron with large negative energy. On account of the virial theorem $E\approx-\langle p^2/2\rangle$ and the last term accounts for the $-E^2/2c^2$ error of the ZORA eigenvalues. The c^{-2} term in the first order regular approximation corrects for this error

$$\tilde{H}_1=-\frac{1}{2}\,H_0\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{c^2}{(2c^2-V)^2}\,\boldsymbol{\sigma}\cdot\mathbf{p}+\text{c.c.}\approx-E\,\frac{p^2}{4c^2}\,. \tag{53}$$

In contrast to the free particle [case (a)], we expect the ZORA eigenvalues to be more negative in this case than the Dirac eigenvalues and the FORA correction to be positive, i.e., of opposite sign compared to the Pauli type correction.

Having considered case (b) in Ref. 7, we present here results for the hydrogenic ion U^{91+} in order to examine the performance of the regular approximation in the case of both high energy and strong Coulombic potential. Table I compares the exact eigenvalues of the Dirac equation with, on the one hand, the zeroth and first order regular approximations and, on the other hand, the nonrelativistic (NR) and Pauli energies. All of these energies can be obtained analytically. The eigenvalues E^D of the Dirac equation are given by

$$E^D=c^2\left[1+\frac{(Z\alpha)^2}{(n-j-\frac{1}{2}+\sqrt{(j+\frac{1}{2})^2-(Z\alpha)^2})^2}\right]^{-1/2}-c^2, \tag{54}$$

TABLE I. Orbital energies of uranium 91+.

Orbital	Dirac	ZORA	FORA	NR	Pauli
$1s_{1/2}(1s)$	−4861.2	−5583.9	−4753.7	−4232.0	−4708.9
$2s_{1/2},2p_{1/2}(2s)$	−1257.39	−1300.95	−1255.88	−1058.00	−1207.02
$2p_{3/2}$	−1089.61	−1122.17	−1088.64		−1087.80
$3s_{1/2},3p_{1/2}(3s)$	−539.09	−546.94	−538.98	−470.22	−523.21
$3p_{3/2},3d_{3/2}$	−489.04	−495.49	−488.95		−487.88
$3d_{5/2}$	−476.262	−482.378	−476.183		−476.109
$4s_{1/2},4p_{1/2}(4s)$	−295.257	−297.597	−295.239	−264.500	−288.715
$4p_{3/2},4d_{3/2}$	−274.408	−276.427	−274.393		−273.814
$4d_{5/2},4f_{5/2}$	−268.966	−270.906	−268.952		−268.846
$4f_{7/2}$	−266.389	−268.292	−266.376		−266.363
$5s_{1/2},5p_{1/2}(5s)$	−185.485	−186.405	−185.480	−169.280	−182.250
$5p_{3/2},5d_{3/2}$	−174.945	−175.763	−174.941		−174.621
$5d_{5/2},5f_{5/2}$	−172.155	−172.948	−172.152		−172.078
$5f_{7/2},5g_{7/2}$	−170.829	−171.609	−170.825		−170.806
$6s_{1/2},6p_{1/2}(6s)$	−127.093	−127.525	−127.092	−117.556	−125.282
$6p_{3/2},6d_{3/2}$	−121.057	−121.449	−121.056		−120.867
$6d_{5/2},6f_{5/2}$	−119.445	−119.826	−119.444		−119.395
$7s_{1/2},7p_{1/2}(7s)$	−92.441	−92.669	−92.440	−86.367	−91.333

where n and $\kappa=\pm(j+\frac{1}{2})$ are the usual quantum numbers of the particular orbital and $\alpha=1/c\approx1/137.037$. Here we only used the positive total energy eigenvalues, from which we subtracted the rest mass energy in order to compare them with nonrelativistic eigenvalues. The ZORA eigenvalues are related to the Dirac ones according to Eq. (9)

$$\tilde{E}_0=\frac{2c^2E^D}{2c^2+E^D}\,. \tag{55}$$

The first order result is [see Eq. (32)]

$$\tilde{E}_{\text{FO}}=\tilde{E}_0+\frac{(\tilde{E}_0)^2}{2c^2}\,. \tag{56}$$

The nonrelativistic (NR) eigenvalues are well known to be

$$E^{\text{NR}}=-\frac{Z^2}{2n^2}\,. \tag{57}$$

If we expand Eq. (54) up to first order in c^{-2} we get the first order energies, which we call Pauli energies E^{Pauli}

$$E^{\text{Pauli}}=E^{\text{NR}}-\frac{(E^{\text{NR}})^2}{2c^2}\left(\frac{4n}{j+\frac{1}{2}}-3\right). \tag{58}$$

Let us first note that the energies in Table I are very large compared to the typical valence energy of ca. 0.5 a.u. Given the $-E^2/2c^2$ error in the ZORA energies, this is not a favorable situation for the zeroth order regular approximation. Still, even at the high energies of this example the ZORA energies for the core-penetrating s and p orbitals are usually superior to Pauli energies. This is true down to an energy of 500 a.u. (the $n=3$ shell). It is only in the very deep core (note, in particular, the $1s_{1/2}$ with an energy close to 5000 a.u.) that ZORA starts to perform poorly. In that case it becomes important to include the first order corrections. Of course, in all cases (including $1s_{1/2}$) the FORA energies are superior to the Pauli energies.

In connection with the relation between relativistic effects and the singularity of the Coulomb potential,[8] it is in-

teresting to consider the differences between the orbitals with different angular momentum belonging to one shell. Orbitals with high angular momentum are much less core penetrating than orbitals with low angular momentum (cf. plots in Ref. 8). This implies that for d, f, and g orbitals the balance between case (a) effects (relatively flat potential, high energy) and case (b) effects (Coulombic singularity) may shift more towards (a), and we observe in Table I that indeed the Pauli results are better in those cases than the ZORA results. This is in contrast to the superiority of ZORA over Pauli for the core penetrating s levels. The p has hybrid behavior: since the zeroth order regular approximate Hamiltonian has spin–orbit coupling and has therefore the same degeneracy in the eigenvalues as the Dirac Hamiltonian, the $p_{1/2}$ levels have the same behavior as $s_{1/2}$ and the $p_{3/2}$ levels the same as $d_{3/2}$.

We may also relate the different behavior of the high and low momentum orbitals of a given shell to the differences they exhibit in the magnitude of the relativistic shift (the difference Dirac–NR). All levels have a downward relativistic shift, but the core penetrating low angular momentum orbitals are by far the largest, in complete accordance with all previous arguments. This implies that the nonrelativistic energy of the shell, E_n^{NR}, is above all the Dirac energies of the shell, and closest to the high angular momentum levels. On the other hand, the ZORA energies are all below the Dirac energies by roughly the same amount (approximately $-E_n^2/2c^2$, much smaller than the spin–orbit splitting). As a corollary, the ZORA energy improves much over the nonrelativistic energy for the low l orbitals but relatively little for the high l ones. The Pauli corrections are not able to recover the large error in the nonrelativistic energy for the low l orbitals, making the ZORA energies superior to the Pauli energies, but for the high l orbitals the Pauli corrections pick up almost completely the relatively small relativistic shift and lead to better results for those orbitals than ZORA.

We finally note that the Pauli corrections lower the energies, in agreement with the dominant mass-velocity contribution $-p^4/8c^2$ which is negative, i.e., causes a fast moving relativistic particle with momentum p to have a smaller kinetic energy than a nonrelativistic particle with the same momentum. The first order correction in the regular approximation can be identified with the mass-velocity correction in case of a free particle [cf. case (a) above] but has the opposite sign for bound particles in a Coulomb potential, [cf. case (c) above]. The dominant contribution to the FORA correction is given by $-Ep^2/4c^2$ which is a positive correction for a bound particle. From Table I it is evident that the FORA corrections are indeed always positive. Evidently, the direction in which the FORA correction works is different for free and bound particles and does not have the same physical interpretation in the two cases.

Let us turn now to the scalar relativistic equations. We were not able to solve Eq. (33) or (34) analytically for orbitals with quantum number $l \neq 0$. For $l=0$ these are just the same equations as the corresponding fully relativistic ones. In Table II we list some numerically calculated eigenvalues in the case of hydrogen-like uranium ($Z=92$). One can compare these with the nonrelativistic eigenvalues and the scalar

TABLE II. Orbital energies of uranium 91+.

	SR	ZORA SR	FORA SR	NR	Pauli SR
$2p$	−1130.34	−1165.41	−1129.25	−1058.00	−1127.54
$3p$	−501.341	−508.124	−501.250	−470.222	−499.658
$3d$	−481.142	−487.386	−481.061	−470.222	−480.819
$4p$	−279.581	−281.677	−279.565	−264.500	−278.781
$4d$	−271.046	−273.016	−271.031	−264.500	−270.833
$4f$	−267.478	−269.396	−267.464	−264.500	−267.427
$5p$	−177.576	−178.419	−177.571	−169.280	−177.164
$5d$	−173.222	−174.025	−173.219	−169.280	−173.095
$5f$	−171.389	−172.174	−171.384	−169.280	−171.351
$6p$	−122.571	−122.972	−122.569	−117.556	−122.339
$6d$	−120.062	−120.447	−120.061	−117.556	−119.984

relativistic Pauli energies, which are given by (for $l>0$)

$$E^{\text{Pauli SR}} = E^{\text{NR}} - \frac{(E^{\text{NR}})^2}{2c^2}\left(\frac{4n}{l+\frac{1}{2}} - 3\right). \tag{59}$$

The eigenvalues belonging to the bound solutions of the Klein–Gordon equation (40) are well known to be

$$E^{\text{KG}} = c^2\left[1 + \frac{(Z\alpha)^2}{(n-l-\frac{1}{2}+\sqrt{(l+\frac{1}{2})^2-(Z\alpha)^2})^2}\right]^{-1/2} - c^2. \tag{60}$$

From Eqs. (47) and (48) we find the zeroth and first order regular approximate KG energies for this problem

$$\tilde{E}_0^{\text{KG}} = \frac{2c^2 E^{\text{KG}}}{2c^2 + E^{\text{KG}}}, \tag{61}$$

$$\tilde{E}_{\text{FO}}^{\text{KG}} = \tilde{E}_0^{\text{KG}} + \frac{(\tilde{E}_0^{\text{KG}})^2}{2c^2}. \tag{62}$$

Equation (40) has no solutions for s orbitals if $Z>c/2$ and thus not for $Z=92$.

The exact eigenvalues of the zeroth order extended Klein–Gordon Hamiltonian $H_0^{\text{ext KG}}$ are

$$E_0^{\text{ext KG}} = \frac{2c^2(1-\Lambda)}{\zeta(1+\Lambda)}, \tag{63}$$

where Λ is given by

$$\Lambda = \left[1 + \frac{\zeta(Z\alpha)^2}{(n-l-\frac{1}{2}+\sqrt{(l+\frac{1}{2})^2-(Z\alpha)^2})^2}\right]^{1/2}. \tag{64}$$

For $\zeta = 1$ these are just the ZORA KG eigenvalues. One can compare these eigenvalues for arbitrary ζ with the exact KG eigenvalues. For $\zeta = \frac{3}{2}$ the difference is minimal and is then of order c^{-4}. For comparison we have shown in Table III some eigenvalues of the Klein–Gordon equation belonging to some orbitals with $l>0$ in the case of $Z=92$. In fact, the expansion of the Klein–Gordon energy in c^{-2} gives in first order the scalar relativistic Pauli energy (for $l>0$). We can follow the same arguments, that were used to explain Table I, to understand the results of Tables II and III.

TABLE III. Orbital energies of uranium 91+.

	Klein–Gordon	ZORA KG	FORA KG	Ext KG
$2p$	−1136.05	−1171.49	−1134.95	−1137.32
$3p$	−503.215	−510.049	−503.123	−503.327
$3d$	−481.236	−487.482	−481.154	−481.333
$4p$	−280.388	−282.497	−280.372	−280.408
$4d$	−271.091	−273.062	−271.076	−271.108
$4f$	−267.483	−269.402	−267.470	−267.501
$5p$	−177.992	−178.839	−177.988	−177.997
$5d$	−173.246	−174.049	−173.243	−173.251
$5f$	−171.393	−172.178	−171.389	−171.397
$6p$	−122.811	−123.214	−122.810	−122.813
$6d$	−120.077	−120.462	−120.075	−120.078

As a last comparison we now look at the radial behavior of some of the solutions we have found for a particle in a Coulomb potential near the origin

$$\begin{aligned}
&\phi^D,\chi^D,\tilde{\Phi}_0 (j=l-1/2)\sim r^{\sqrt{l^2-Z^2/c^2}-1},\\
&\phi^D,\chi^D,\tilde{\Phi}_0 \ \ (j=l+1/2)\sim r^{\sqrt{(l+1)^2-Z^2/c^2}-1},\\
&\phi^{\mathrm{SR}},\tilde{\phi}_0^{\mathrm{SR}}\sim r^{\sqrt{l(l+1)+1-Z^2/c^2}-1},\\
&\Psi^{\mathrm{KG}},\tilde{\Phi}_0^{\mathrm{KG}}\sim r^{\sqrt{(l+1/2)^2-Z^2/c^2}-1/2},\\
&\Psi^{\mathrm{NR}}\sim r^l.
\end{aligned} \tag{65}$$

Here χ^D is the small component of the Dirac spinor and $\gamma=\sqrt{1-Z^2/c^2}$. In all cases the regular approximate form has the right behavior. Here we can see that the ZORA solution has the same mild singularity at the origin as the Dirac solution. In fact, near the nucleus the radial behavior of the ZORA solution is the same as that of the large component of the Dirac wave function, because only a scaling has been applied. This was to be expected, because the regular expansion parameter $E/(2c^2-V)$ tends to zero near the origin. The ZORA orbital is slightly more contracted than the Dirac one. In Ref. 7 some figures are shown, coming from all-electron calculations, which show that the ZORA orbital electron densities are very close to the Dirac orbital densities, i.e., pick up the relativistic orbital contraction very accurately. A nice feature of the regular approximations is that already in zeroth order they distinguish between expansions of the Dirac, Klein–Gordon, and scalar relativistic equation. Of course, in all these three cases the c^{-1} expansion of these equations in zeroth order are identical, namely the Schrödinger equation.

From Tables II and III we can see that the larger the l value, the more the eigenvalues of the Klein–Gordon and the scalar relativistic Hamiltonian look the same. The reason for this can be seen if we consider the difference between for example the regular approximate form of these Hamiltonians

$$\begin{aligned}
\tilde{H}_0^{\mathrm{KG}}-\tilde{H}_0^{\mathrm{SR}}&=\frac{c}{\sqrt{2c^2+\frac{Z}{r}}}\left(p^2\frac{c}{\sqrt{2c^2+\frac{Z}{r}}}\right)\\
&=-\frac{3c^2Z^2}{4r(2c^2r+Z)^3}\,.
\end{aligned} \tag{66}$$

Near the origin this difference looks like a Coulomb potential, but for larger r it goes rapidly to zero. Therefore the difference is most important for s orbitals. One can also look at the radial behavior of the eigenfunctions near the origin according to Eq. (65) to see that the higher the l, the less important the difference. Because the difference is negative we can understand why the eigenvalues of the Klein–Gordon equation are lower than the eigenvalues of the scalar relativistic equation. In fact, this difference is the reason that the ZORA KG Hamiltonian is already not bounded from below for $Z>c/2$ instead of $Z>c$ as is the case for the ZORA SR Hamiltonian.

VIII. CONCLUSIONS

In this paper an exact relation has been found between the Dirac equation and the zeroth order regular approximate (ZORA) equation for hydrogen-like atoms. This relation was found by a method of energy-dependent scaling of coordinates. The negative energy spectrum of the Dirac Hamiltonian is shown to be transferred to a positive energy continuum in the ZORA case. As a consequence it is proven that the ZORA Hamiltonian is bounded from below for attractive Coulomb-like potentials, under the restrictions that none of the point charges Z may be larger than $c\approx 137.037$, and the potential is everywhere smaller than $2c^2$. These restrictions are almost always fulfilled for a mean field kind of theory of electrons in atoms, molecules, or solids. The ZORA Hamiltonian is therefore an attractive approximation to the Dirac Hamiltonian. Similar to the derivation of virial theorems by scaling of coordinates, an exact result for the first order regular approximate energy can be derived in the case of hydrogen-like atoms. From the exact results for the hydrogen-like atoms one may note the following properties of the regular approximations: (a) to first order the results of the regular approximation are always superior to the Schrödinger plus Pauli results; (b) for low-energy electrons that move in a strong Coulomb potential (such as the core-penetrating valence s and p electrons) already the ZORA is much better than the Pauli approximation; (c) high angular momentum orbitals, that avoid the nuclear region, have a relatively small relativistic effect and a relatively accurate Pauli result, usually better than ZORA but inferior to FORA. These findings are in accordance with the results of Ref. 8, where it has been stressed that the relativistic effects of electrons moving in a Coulombic potential originate from the nuclear neighborhood.

These conclusions for the hydrogenic ion do not hold unmodified for many-electron atoms. In particular, high angular momentum orbitals do have large relativistic effects in that case, which are however indirect: the self-consistent-field (SCF) potentials change due to relativistic changes in other orbitals.[8] Therefore, already the SCF ZORA results,

that do contain these effects, are superior to Pauli results for all the valence orbitals of heavy elements, including the d and f levels.[7]

Expansions in $E/(2c^2 - V)$ of scalar relativistic equations, like the Klein–Gordon equation, were used to obtain the regular approximate form of these equations. Some of the approximate equations could be solved exactly for one particle in a Coulomb potential of a point charge. A pleasing feature of the regular approximations is that already in zeroth order they distinguish between expansions of the Dirac, Klein–Gordon, and scalar relativistic equation.

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