PHYSICAL REVIEW A VOLUME 38, NUMBER 12 DECEMBER 15, 1988

Relativistically corrected Schrödinger equation

M. Kissel-Phillip and W. H. E. Schwarz
Department of Chemistry, The University, D-5900 Siegen, West Germany

(Received 22 February 1988)

The relativistically corrected Schrödinger (RS) equation $[(m^2c^4+p^2c^2)^{1/2}+V-E]\Psi=0$ is sometimes used to describe charged fermions, which are subject to strong *Zitterbewegung*. Since, however, equations of this type describe bosons with weak *Zitterbewegung* effects, it is mandatory to screen the Coulomb potential V in an r range of order h/mc, and also to add a screened spin-orbit potential. Thereby the singularity problems with Coulomb potentials are avoided. While the Pauli Hamiltonian must not be used in variational or eigenvalue equations, the RS Hamiltonian may be. An effective potential for the RS equation is derived, which yields relativistically corrected energies and wave functions for fermion systems with Coulomb potentials. Accurate numerical solutions for an unshielded single-center Coulomb potential are presented.

I. INTRODUCTION

Relativity plays an important though not dominant role in the valence shells of heavy elements. The same holds in several other fields, for instance, for "onium" systems like quarkonium, hadronium, etc. Relativistic quantum field theory and even the classical Dirac equation are still difficult to apply to many-particle and multicenter problems. For those problems, nonrelativistic approaches with additional corrections in order to account for the relativistic effects in an approximate manner are desirable. They are both conceptually and computationally simpler.

It is common practice to begin with a Schrödinger-type eigenvalue equation (working with two-component spinors in the case of spin-$\frac{1}{2}$ particles). Relativistic kinematics may be accounted for by adding the so-called velocity-mass term $h^{\mathrm{VM}}=-p^4/8m^3c^2$ to the nonrelativistic kinetic energy. The corresponding rather ubiquitous Pauli eigenvalue equation is, however, very ill behaved and has, for instance, no bound states at all. Another popular approach is to use the square-root expression $(m^2c^4+p^2c^2)^{1/2}$ for the relativistic kinetic energy, an approach which is still not completely satisfactory in the case of singular interactions, e.g., the Coulomb potential $V=-Z/r$.

These approaches are at best suited for bosonic systems. For fermions, the potential energies have to be corrected also, even at the lowest order of approximation. Conventionally the Coulomb interaction is corrected by the Pauli-type spin-orbit and Darwin terms $[h^{\mathrm{SO}}=(Z/2c^2r^3)\mathbf{l}\cdot\mathbf{s},\ h^{D}=(Z\pi/2m^2c^2)\delta(r)]$. As in the case of the velocity-mass correction h^{VM}, they must not be used in variational eigenvalue equations, but only in first-order perturbation theory. Furthermore, it should be noted that h^{VM} is only valid for $p<mc$, and h^{SO} and h^{D} only for $r>Z/mc^2$. Thus, potential corrections are needed which are applicable in the *inner regions* of the very deep Coulomb potentials.

The shift of the total energy due to the relativistic correction of kinetic and potential contributions leads to a significant shift of the classical turning points, if the potential gradient is small. This is, for instance, the case for the outer turning point in a Coulomb potential. Although the particle moves there with nonrelativistically low velocity, its motion is appreciably modified. Many phenomena in atomic, molecular, and solid-state physics depend sensitively on the wave function in the *outer region*, i.e., in the "chemically active" valence shell. Therefore it is important to have an approach which simultaneously yields both reasonably accurate energies and wave functions.

Our aim is to develop a variational two-component eigenvalue equation for multicenter multiparticle systems. The first step is to improve on the Pauli-type one-particle potential corrections mentioned above. These corrections may easily be developed for solvable one-particle one-center systems, and may then be adapted to more general cases (for instance, to molecular self-consistent field problems). A relativistically corrected Schrödinger one-particle model Hamiltonian is made plausible in Sec. II. The form and the coefficients of a model potential appropriate for the Coulomb interaction are determined analytically in Sec. III. Numerical results for this model of hydrogenlike atoms are presented in Sec. IV. The results are summarized and discussed in Sec. V. In the Appendix we comment on the pure Coulomb square-root case and on the velocity-mass term.

II. RELATIVISTICALLY CORRECTED SCHRÖDINGER EQUATION

Significant progress has been achieved in deriving *rigorous* two-component formalisms in the configuration space of N electrons.[1-6] In general the equations define an effective Hamiltonian in an implicit and rather involved form. They have successfully been implemented on the computer, but they are not specially suited for interpretative purposes because of their complexity. On the other hand, *Pauli-type* equations (though conceptually not being completely satisfactory) have also been implemented successfully within the frameworks of the $X\alpha$

and the pseudopotential approaches.[7–12] Here we shall develop a model Hamiltonian at an *intermediate* level.

The classical relativistic energy expression for a free particle may be written in three nearly equivalent forms, namely,

$$(m^2c^4+p^2c^2)^{1/2}=E\ , \tag{1a}$$

$$m^2c^4+p^2c^2=E^2\ , \tag{1b}$$

or

$$\beta mc^2+\boldsymbol{\alpha}\cdot\mathbf{p}c=E\ . \tag{1c}$$

After introducing an external scalar potential U (which modifies the effective mass) and a four-vector potential $(\mathbf{A},V)$, according to the minimal coupling rule one obtains

$$[(mc^2-U)^2+(\mathbf{p}c-\mathbf{A})^2]^{1/2}=(E-V)\ \ (\mathrm{RS})\ , \tag{2a}$$

$$(mc^2-U)^2+(\mathbf{p}c-\mathbf{A})^2=(E-V)^2\ \ (\mathrm{KG})\ , \tag{2b}$$

or

$$\beta(mc^2-U)+\boldsymbol{\alpha}\cdot(\mathbf{p}c-\mathbf{A})=(E-V)\ \ (D)\ . \tag{2c}$$

Upon quantization, these equations are no longer equivalent since the p operator and the r-dependent potential operators do not commute. This is seen most clearly in the following equivalent formulations:

$$\{m^2c^4+p^2c^2-(E^{\mathrm{RS}}-V)^2+[(m^2c^4+p^2c^2)^{1/2},V(r)]_-\}\Psi^{\mathrm{RS}}=0\ , \tag{3a}$$

$$[m^2c^4+p^2c^2-(E^{\mathrm{KG}}-V)^2]\Psi^{\mathrm{KG}}=0\ , \tag{3b}$$

$$\{m^2c^4+p^2c^2-(E^{D}-V)^2+[\boldsymbol{\alpha}\cdot\mathbf{p}c,V(r)]_-\}\Psi^{D}=0\ . \tag{3c}$$

From here on we have assumed $U=0$ and $\mathbf{A}=0$. The corresponding relativistic energy corrections of the positive-energy ground states for the case $V=-Z/r$, as a function of Z, are shown in Fig. 1. If $E_{1s}(Z)$ is expanded as $\sum_i a_i c^2 (Z/c)^i$, the leading coefficient of the relativistic correction a_4 is given by $\Delta(Z=0)$ in Fig. 1, and a_5 is given by the slope $(d\Delta/dZ)_{Z=0}$. Bound states are only obtained for Z values below some bounds,[13] which are indicated in Fig. 1 by dashed vertical lines.

The correct wave equations for spin-0 and spin-$\frac{1}{2}$ particles are the Klein-Gordon (KG) and the Dirac (D) equations, (2b) and (3b) and (2c) and (3c), respectively. The so-called relativistically corrected Schrödinger (RS) or square-root equation (2a) and (3a) exhibits the similarity with the classical relativistic energy expression (1a) and with the conventional Schrödinger equation

$$(mc^2-U)+(\mathbf{p}c-\mathbf{A})^2/2(mc^2-U)=(E-V) \tag{4}$$

in the most direct manner.

Some aspects of these three equations can be understood more easily, if they are written in two-component particle-antiparticle form. We have found that

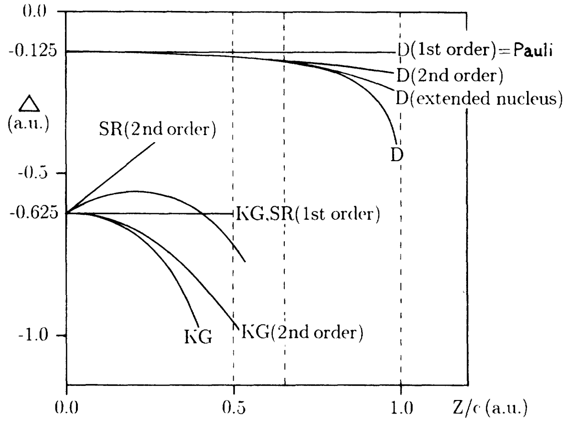

FIG. 1. Relativistic energy corrections with respect to the Schrödinger energy E^{Schr}: $\Delta=(E^{\mathrm{rel}}-E^{\mathrm{Schr}})c^2/Z^4$ for the hydrogenic ground state vs Z/c, from the Dirac (D), square-root (SR), and Klein-Gordon (KG) equations.

$$\begin{bmatrix} mc^2+R+V-E^{\mathrm{RS}} & R \\ R & mc^2+R-V+E^{\mathrm{RS}} \end{bmatrix}\begin{bmatrix}\Psi_+^{\mathrm{RS}}\\ \Psi_-^{\mathrm{RS}}\end{bmatrix}=0 \tag{5a}$$

is equivalent with Eqs. (2a) and (3a), where $\Psi^{\mathrm{RS}}=\Psi_+^{\mathrm{RS}}+\Psi_-^{\mathrm{RS}}$ and

$$R=p^2/2m+[\{1+(p/mc)^2\}^{1/2},V]_-\ . \tag{6}$$

Equation (5a) can be derived in a similar way as the Feshbach-Villars representation of the Klein-Gordon equation,[2]

$$\begin{bmatrix} mc^2+T+V-E^{\mathrm{KG}} & T \\ T & mc^2+T-V+E^{\mathrm{KG}} \end{bmatrix}\begin{bmatrix}\Psi_+^{\mathrm{KG}}\\ \Psi_-^{\mathrm{KG}}\end{bmatrix}=0\ , \tag{5b}$$

where $T=p^2/2m$. Equation (5b) has the same structure as the standard representation of the Dirac equation, written explicitly as

$$\begin{bmatrix} mc^2+V-E^{D} & c(\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}) \\ c(\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}) & mc^2-V+E^{D} \end{bmatrix}\begin{bmatrix}\Psi_+^{D}\\ \Psi_-^{D}\end{bmatrix}=0\ . \tag{5c}$$

Of course, $\Psi_\pm^D$ are two-component spinors.

The diagonal terms of the *Klein-Gordon equation* (5b) are the nonrelativistic energies (of order mc^2) of particle and antiparticle with frequency factor E and energy $\mathcal{E}=|E|$. The off-diagonal $p^2/2m$ coupling is of order c^0 so that the lower component of a particle state is of order c^{-2}. Thus the relativistic corrections become of even order in c, the leading one for the kinetic energy being of order c^{-2}, and for the potential energy being of order c^{-4}.

The RS equation (5a) differs from the KG equation (5b) in two respects. First, the diagonal potential $(\sigma_z V)$ is modified by a commutator of V with the square-root operator [i.e., with terms of order (p/c) in the region of large p; and of order $(p/c)^2$ in the region of small p]. Second, the off-diagonal coupling is similarly modified. Consequently, the V-dependent relativistic energy corrections will contain terms of even and odd powers of c, starting with c^{-3}.

Upon linearization, one obtains the *Dirac equation* (5c) with off-diagonal p coupling of order c^1, so that the lower component becomes of order c^{-1}. Consequently V-dependent relativistic corrections already appear in the order of c^{-2}. We note that a linear momentum vector $\mathbf{p}^1$ in the Hamilton equation implies spin (both in the relativistic *and* nonrelativistic theories[14], but a linear momentum value $|p|^1$ does not. For instance, substitute $ic|p|$ for $c(\boldsymbol{\sigma}\cdot\nabla)$ in Eq. (5c). This is an equation without spin, but with a spin-independent potential correction of order c^{-2}.

Summarizing, the coupling of the upper and lower components in the Feshbach representations (5) is of order $k=(p/2mc)$ or $k=(p/2mc)^2$ for an equation with linear or quadratic momentum, respectively. The transformation to a pure free-particle basis is represented by a matrix of the form

$$F\sim\begin{bmatrix}1+O(k^2) & O(k)\\ O(k) & 1+O(k^2)\end{bmatrix}=1+\sigma_x\times O(k)+O(k^2)\ . \tag{6}$$

The potential, which a pure free particle feels, is thus

$$V^{\text{eff}}=F^{-1}(\sigma_z V)F \tag{7}$$

$$=V[\sigma_z+\sigma_x\times O(k)+\sigma_z\times O(k^2)+\cdots]\ , \tag{8}$$

where the odd operator σ_x couples upper and lower components [differing by order $O(k^1)$]. Therefore the potential energy contains relativistic correction terms of order k^2. That is of order $(p/2mc)^2$ or $(p/2mc)^4$ if the momentum is linear as in Eq. (5c) or quadratic as in Eq. (5b), respectively. These are the so-called *Zitterbewegung* corrections. The different behavior of the eigenvalues of the RS and KG equations (5a) and (5b), on one hand, and of the D equation (5c), on the other hand, is exhibited in Fig. 1. Consequently, if a Schrödinger-type equation (containing p^2) is to be used to simulate energies and densities of the Dirac equation (containing $\mathbf{p}^1$), σ-, p-, and V-dependent modification terms of order c^{-2} have to be added, yielding an effective potential V^{eff}. In other words, the relativistically corrected Schrödinger equation should be of the form

$$[(m^2c^4+p^2c^2)^{1/2}+V^{\text{eff}}-E^{\text{eff}}]\Psi^{\text{eff}}$$

$$=(H^{\text{eff}}-E^{\text{eff}})\Psi^{\text{eff}}=0\ . \tag{9}$$

We note that in a more general approach one might also add U^{eff} and $\mathbf{A}^{\text{eff}}$ terms to the mass and momentum terms under the square root. For instance, it has been shown that the *Zitterbewegung* correction can also be simulated by a scalar potential U with $U\rightarrow0$ for $r\rightarrow\infty$ and $U\rightarrow-\text{const}\times Zc^{-2}$ for $r\rightarrow0$.[15]

III. EFFECTIVE MODEL POTENTIAL FOR COULOMB SYSTEMS

A. Plausible ansatz for V^{eff}

For a constant potential $V=V_0$, any type of transformation procedure from the Dirac equation to a two-component formalism[1–4] yields Eq. (9) with $V^{\text{eff}}=V_0$. We note that for very small $r\rightarrow0$ any realistic potential V of an extended nucleus goes like $V\rightarrow V_0$, which, however, does not imply $V^{\text{eff}}\rightarrow V_0$.

For large r, corresponding to small p, the nuclear potential $V=-Z/r$ is weak. Then the conventional Pauli approximation is applicable. V^{eff} consists of V and of the spin-orbit term $\sim\mathbf{l}\cdot\mathbf{s}/r^3$. The Darwin term $\sim\delta(r)$ vanishes for large r. The velocity-mass term $\sim p^4$ is just the low-p first-order correction of the square root in Eq. (9) to the nonrelativistic kinetic energy.

For small r, corresponding to large p, the different decoupling procedures for the Dirac equation all yield pc for the kinetic energy. This is the leading term of the square root of Eq. (9) for large momenta. The spin-independent leading term for the potential becomes $V^{\text{eff}}\approx(V+\hat{\mathbf{p}}V\cdot\hat{\mathbf{p}})/2$, where $\hat{\mathbf{p}}=\mathbf{p}/p$.[3] That is, V^{eff} is obtained by smearing or averaging V a bit. The leading spin-dependent term for $V=-Z/r$ is $V_{ls}\sim V\mathbf{l}\cdot\mathbf{s}$.

The following ansatz interpolates between the large-r and small-r behavior:

$$V^{\text{eff}}=-Z\times\begin{cases}1/r & \text{for } r\geq R_0\\ a-br^2 & \text{for } r\leq R_0\end{cases}$$

$$+Z(\mathbf{l}\cdot\mathbf{s}/2c^2)\times\begin{cases}1/r^3 & \text{for } r\geq R_{ls}\\ (f/r)-g & \text{for } r\leq R_{ls}\ .\end{cases} \tag{10}$$

We note that our strategy differs from the one of Karwowski and Kobus,[16] who do not require the potential to behave correctly asymptotically. Our V^{eff} is a local approximation to the "effective Hamiltonian" of Chang *et al.*[4]

B. Analytical determination of the parameters

The condition of smooth continuity at R_0 and R_{ls} fixes the parameters a, b, f, and g,

$$a=3/2R_0,\quad f=3/R_{ls}^2\ ,$$

$$b=1/2R_0^3,\quad g=2/R_{ls}^3\ , \tag{11}$$

The remaining parameters R_0 and R_{ls} can be determined analytically through the requirement that for low nuclear charges the model energy E^{eff} of hydrogenlike atoms should coincide at some order of perturbation theory (with respect to the nonrelativistic Schrödinger Hamiltonian as H_0) with the Dirac values E^D,

$$E_{nk}^D=c^2/[1+(Z/c\gamma)^2]^{1/2}$$

$$\text{with } \gamma=n-k+(k^2-Z^2/c^2)^{1/2}\ , \tag{12}$$

where we have assumed $m=1$. Specifically, for 1s

$$E_{11}^D=c^2-Z^2/2-Z^4/8c^2+O(Z^6/c^4)\ , \tag{13a}$$

for $2s,p_{1/2}$

$$E_{21}^D=c^2-Z^2/8-5Z^4/128c^2+O(Z^6/c^4)\ , \tag{13b}$$

and for $2p_{3/2}$

$$E_{22}^D=c^2-Z^2/8-Z^4/128c^2+O(Z^6/c^4)\ . \tag{13c}$$

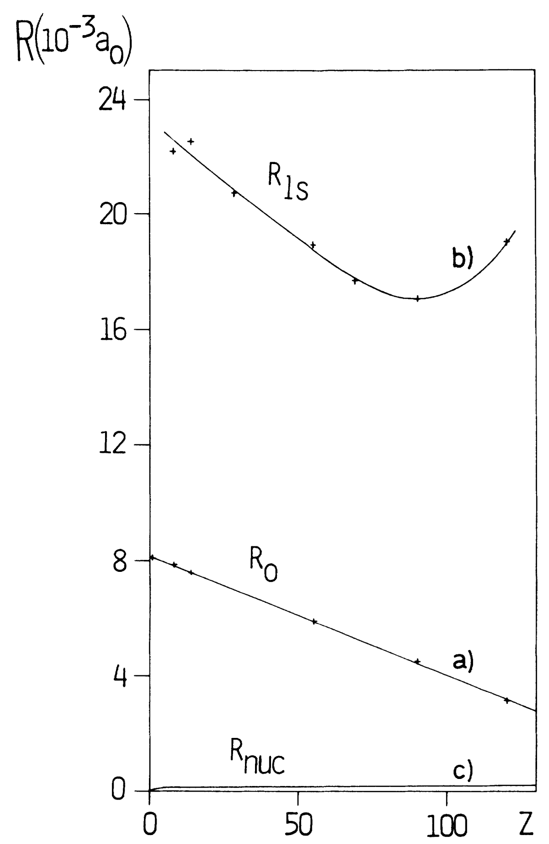

FIG. 2. R parameters of Eqs. (10) and (16) in units of $10^{-3}a_0$ vs nuclear charge. (a) R_0 fitted to the $1s_{1/2}$ Dirac energies, (b) R_{ls} fitted to the $2p_{1/2}$ Dirac energies, and (c) nuclear radius $R_{\text{nuc}} \approx (M)^{1/3}/2c^2$ (Ref. 30).

First-order perturbation theory yields

$$\langle 1s_{1/2}|H^{\text{eff}}|1s_{1/2}\rangle = c^2 - Z^2/2 - Z^4(5/8c^2 - 2R_0^2/5) + O(Z^5R_0^3, Z^5/c^3) , \tag{14a}$$

$$\langle 2s_{1/2}|H^{\text{eff}}|2s_{1/2}\rangle = c^2 - Z^2/8 - Z^4(13/128c^2 - R_0^2/20) + O(Z^5R_0^3, Z^5/c^3) , \tag{14b}$$

$$\langle 2p_{1/2}|H^{\text{eff}}|2p_{1/2}\rangle = c^2 - Z^2/8 - Z^4(7/384c^2 + 1/48c^2) + O(Z^6R_0^4, Z^6/c^4, Z^6R_{ls}^4) , \tag{14c}$$

$$\langle 2p_{3/2}|H^{\text{eff}}|2p_{3/2}\rangle = c^2 - Z^2/8 - Z^4(7/384c^2 - 1/96c^2) + O(Z^6R_0^4, Z^6/c^4, Z^6R_{ls}^4) . \tag{14d}$$

Comparison of (13a) with (14a) or of (13b) with (14b) yields the consistent first-order expression for R_0,

$$R_0 = \sqrt{5}/2c + O(Z/c^2) . \tag{15a}$$

Similarly (13b) and (14c) and (13c) and (14d) both yield

$$R_{ls} = O(1/c) . \tag{15b}$$

The next higher terms may be obtained by second-order perturbation theory which, however, is far from trivial. The coefficients have been determined by numerical techniques. The results are (compare also Fig. 2)

$$R_0 = c^{-1}[\sqrt{5}/2 - 0.75(Z/c)] , \tag{16a}$$

$$R_{1s} = c^{-1}f(Z/c) \approx c^{-1}[3.2 - 1.7(Z/c) + 1.5(Z/c)^4] . \tag{16b}$$

IV. NUMERICAL RESULTS

Equation (9) with $V = -Z/r$ (see Appendix) and with V^{eff} [Eqs. (10), (11), and (16)] has been solved by the basis-set-expansion method using 25 to 30 even tempered optimized Cartesian Gaussians. All matrix elements were calculated analytically including those of the square-root operator, which were determined exactly in p space by using Fourier-transform techniques.[17,18]

In Table I the relativistic energy corrections $(E^{\text{Schr}} - E^{\text{rel}})$ of the Pauli approximation, our model, and the Dirac approach are compared for hydrogenic $1s_{1/2}$, $2s_{1/2}$, $2p_{1/2}$, $2p_{3/2}$, and $3s_{1/2}$ states. E^{Schr} is the nonrelativistic Schrödinger energy. On the average there is an improvement over the Pauli first-order perturbational results, the main advantage, however, being the variational character of the model approach.

Therefore we can directly determine relativistically

TABLE I. Relativistic energy correction $(E^{\text{Schr}} - E^{\text{rel}})c^2/Z^4$ of hydrogenlike ions. E^{rel} has been calculated with the Pauli approximation, the present model, and the Dirac approach.

Z	Method	$1s_{1/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$	$3s_{1/2}$
8	Pauli	0.125	0.0391	0.0391	0.0078	0.0139
8	Eq. (8)	0.125	0.0392	0.0391	0.0078	0.0139
8	Dirac	0.125	0.0391	0.0391	0.0078	0.0139
55	Pauli	0.125	0.0391	0.0391	0.0078	0.0139
55	Eq. (8)	0.136	0.0402	0.0427	0.0076	0.0142
55	Dirac	0.136	0.0427	0.0427	0.0080	0.0151
90	Pauli	0.125	0.0391	0.0391	0.0078	0.0139
90	Eq. (8)	0.162	0.0449	0.0515	0.0075	0.0155
90	Dirac	0.162	0.0515	0.0515	0.0083	0.0178

TABLE II. Relative relativistic orbital contraction 100 $(r^{\text{Schr}}-r^{\text{rel}})/r^{\text{Schr}}(c/Z)^2$. Model values (Dirac values in parentheses) of hydrogenic orbitals.

	Z	$1s_{1/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$	$3s_{1/2}$
r^2	8	82(58)	68(67)	79(79)	20(18)	53(53)
r^2	55	78(59)	67(68)	79(79)	22(18)	52(53)
r^2	90	73(62)	63(68)	79(79)	21(19)	50(55)
r^1	8	50(33)	36(37)	43(44)	13(10)	26(28)
r^1	55	46(35)	36(38)	44(45)	12(10)	26(29)
r^1	90	44(38)	36(40)	47(48)	12(10)	28(31)
$-r^{-1}$	8	90(50)	82(63)	63(63)	12(12)	63(50)
$-r^{-1}$	55	66(57)	71(72)	61(72)	15(13)	56(57)
$-r^{-1}$	90	77(76)	74(96)	77(96)	16(14)	58(74)

corrected expectation values from the model wave functions Ψ^{eff}. r^2, r^1, and r^{-1} expectation values in Table II show the relativistic orbital contraction as compared to the nonrelativistic Schrödinger values. There is rough qualitative agreement between our model and the Dirac values.

V. DISCUSSION

The relativistic corrections for the Hamiltonian of a particle in an external field may be divided up into three contributions (using the Schrödinger description as the reference).

(i) In general there is the unique, purely kinetic velocity-mass effect $\sim -p^4/8c^2$, which contributes, e.g., $\sim -5Z^4/8c^2$ to the energy of a hydrogenic 1s state (see the Klein-Gordon result in Fig. 1).

(ii) Furthermore, there are potential-dependent effects, which also depend on the details of the relativistic kinematics. The power of p in the basic Hamiltonian determines the order of $1/c$ of the lower component in the Feshbach representation. The latter determines the transformation F [see Eq. (6)] to free-particle and free-antiparticle states, i.e., it determines the smearing of the position operator for pure particles ($x \rightarrow F^{-1}xF$, the so-called *Zitterbewegung* effect). This in turn determines the order of the correction terms to the effective potential acting on a pure quasiparticle in the field. In the Klein-Gordon case this correction is only of order $1/c^4$, while in the Dirac case it is of order $1/c^2$ (e.g., $+Z^4/2c^2$ for the hydrogenic 1s energy), i.e., it is of the same order as the velocity-mass effect (see Fig. 1).

The square-root case is more complicated. The Hamiltonian contains p^2, as in the Klein-Gordon case, but under the square root. The Taylor expansion of the square root in terms of p^2 has a finite convergence radius. Whether one can make use of the simple p^2 power-expansion behavior depends on the importance of the high-p values, which in turn depends on the potential. For "weakly" attractive potentials [for instance, for a screened Coulomb potential as that given by Eqs. (10), (11), and (16), with $|V| \lesssim c^2$], the high-p values are not dominant and the relativistic potential energy contribution is of order c^{-4}. For an unscreened Coulomb potential, however, this contribution becomes of order c^{-3} (see Appendix and Fig. 1).

(iii) If the momentum appears linearly *and* in explicit vector form in the original Hamiltonian, spin-dependent effects appear. Namely, the different relations emerging for the different components of p can only be fullfilled by multidimensional representations of the Galilei or Lorentz group.

Dirac fermions are characterized, in addition to the relativistic kinetic energy effect, by relativistic potential energy effects [of types (ii) and (iii), both of order c^{-2}]. If one wants to describe fermions (for instance, electrons or quarks) by the "simple" bosonic square-root Hamiltonian (2a) it is necessary to introduce a screening of the original potential, which accounts for the larger *Zitterbewegung* (and also for the spin) of the Dirac fermions. That is, one must introduce the relativistic potential effects for fermions of order c^{-2} explicitly into the square-root equation by an effective model potential and thereby simultaneously eliminate the next higher term of odd order. One must not use an unshielded Coulomb potential when modeling the behavior of charged fermions by the square-root equation. One must also not use the Pauli Hamiltonian for variational calculations despite the fact that the equation $(H^{\text{Pauli}}-E)\Psi=0$ is presented in may textbooks; this equation does not even have a discrete spectrum.[19]

We have here worked out a square-root model equation (9) with screened Coulomb and spin-orbit potentials, which can easily be used in variational calculations of fermionic systems. The effective potential is given by Eqs. (10), (11), and (16). The shielding is of order h/mc. The results are more accurate than those of Pauli first-order perturbation theory. Especially, one easily obtains relativistically corrected wave functions and expectation values. Furthermore, since Eq. (9) is not of the Dirac-Feshbach type with upper and lower components, there do not occur any problems with variational instability.[5] By not explicitly introducting the negative sign of the square root one also easily avoids the continuum dissolution in corresponding many-particle calculations.

ACKNOWLEDGMENT

We are grateful to J. Sucher and G. Hardekopf for the communication of unpublished results, to E. L. Tomusiak for helpful remarks, and to the Deutsche Forschungsgemeinschaft (DFG) and the Ministerium für

Wissenschaft und Forschung von Nordrhein-Westfalen and Fonds der Chemischen Industrie for financial support. We acknowledge the services of the computational centers of the universities of Siegen and Köln.

APPENDIX: SQUARE-ROOT EQUATION WITH UNSCREENED COULOMB POTENTIAL

The square-root equation with unshielded $V=-Z/r$ has been discussed frequently.[13,20–29] Several authors[22,23] have independently derived the same analytical expressions for the energy of $l=0$ states,

$$\begin{aligned}E_{ns}&=c^2/[1+(Z/nc)^2]^{1/2}\\&=c^2-Z^2/2n^2+3Z^4/8n^4c^2-O(Z^6/c^4)\ ,\end{aligned}\tag{17}$$

while Tzara[26] obtained an implicit relation for E^{RS}, which can be shown to differ from (17) by terms of order $-O(Z^5/c^3)$. Numerical results have been published which were said to corroborate Eq. (17),[22] or conversely to agree with the Dirac energies of Eqs. (12) and (13).[24] Equation (17) corresponds to $E^{\mathrm{KG}}<E^{D}<E^{\mathrm{Schr}}<E^{\mathrm{RS}}$, while we have obtained $E^{\mathrm{KG}}<E^{\mathrm{RS}}<E^{D}<E^{\mathrm{Schr}}$ for the appropriately treated Coulomb potential.

The simplest approach is to expand the square-root operator in a Taylor series of $(p/c)^2$ and to apply perturbation theory. In first-order one correctly obtains

$$\begin{aligned}E_{ns}=c^2&-Z^2/2n^2-5Z^4/8n^4c^2\\&+\text{divergent terms of order }Z^6/c^4\ .\end{aligned}\tag{18}$$

This result does not coincide with that of Friar and Tomusiak.[23]

Farazdel and Smith[27] have noted recently that the power expansion of the square root has a finite radius of convergence. They have challenged the usefulness of this expansion and its application even in lowest order of perturbation theory. However, what one may conclude is that the first three terms of an expansion of E_{ns} are correctly recovered by the convergent terms of Eq. (18), and that the remainder cannot be represented by a power series of Z^{2n}/c^{2n-2}.

TABLE III. Power-expansion coefficients for the ground-state eigenvalue of the square-root Coulomb equation. Third digits (in parentheses) may be inaccurate.

Reference	a_4	a_5
21,22,25	$+\frac{3}{8}$	0
26	$+\frac{3}{8}$	$-\frac{1}{6}$
6	$-\frac{5}{8}$	+0.67(0) (numerical)
13	$-\frac{5}{8}$	$+\frac{8}{3}\pi=0.8488$
This work	$-\frac{5}{8}$	+0.84(2) (numerical)

A more successful approach is by explicitly introducing

$$\Delta H=H^{\mathrm{eff}}-H^{\mathrm{Schr}}=(c^4+p^2c^2)^{1/2}-c^2-p^2/2$$

in closed form. First-order perturbation theory for the 1s state in momentum space yields a closed expression in terms of hypergeometric functions.[18] The power expansion of this result yields [compare with Eq. (18)]

$$\begin{aligned}E_{1s}=c^2&-Z^2/2-5Z^4/8c^2+64Z^5/15\pi c^3\\&-35Z^6/16c^4+\cdots\ .\end{aligned}\tag{19}$$

We note that odd powers of c appear, although the square-root Coulomb operator contains c^2 only. Second-order perturbation theory for the 1s state yields an additional energy correction [Hardekopf and Sucher[13] (private communication)] of $-8Z^5/5\pi c^3+O(Z^6/c^4)$, resulting in

$$E_{1s}=c^2-Z^2/2-5Z^4/8c^2+8Z^5/3\pi c^3+O(Z^6/c^4)\ .\tag{20}$$

In order to check this result we have solved Eq. (9) with $V=-Z/r$ numerically, as described in Sec. IV, for a series of Z values. The coefficients a_i in the power expansion $E(Z)=\sum_i a_i c^2(Z/c)^i$ were then determined by fitting to the numerical energies. There is agreement between all authors concerning the first four coefficients: $a_0=1$, $a_2=-\frac{1}{2}$, and $a_1=a_3=0$. Results for the next two coefficients are presented in Table III. The present numerical results corroborate the analytical expansion (20).

---

[1] L. L. Foldy and S. A. Wouthuysen, Phys. Rev. **78**, 29 (1950).

[2] H. Feshbach and F. Villars, Rev. Mod. Phys. **30**, 24 (1958).

[3] M. Douglas and N. M. Kroll, Ann. Phys. (N.Y.) **82**, 89 (1974). E. Eriksen and M. Kolsrud, Suppl. Nuovo Cimento, **18**, 1 (1960).

[4] Ch. Chang, M. Pelissier, and Ph. Durand, Phys. Scr. **34**, 394 (1986).

[5] W. H. E. Schwarz and E. Wechsel-Trakowski, Chem. Phys. Lett. **85**, 94 (1982).

[6] B. A. Hess, Phys. Rev. A **32**, 756 (1985); B. A. Hess, Habilitationsschrift, Universität Wuppertal, 1985; B. A. Hess, Phys. Rev. A **33**, 3742 (1986); B. A. Hess, Phys. Scr. **36**, 412 (1987).

[7] R. D. Cowan and D. C. Griffin, J. Opt. Soc. Am. **66**, 1010 (1976).

[8] W. C. Ermler, Y. S. Lee, K. S. Pitzer, and N. W. Winter, J. Chem. Phys. **69**, 976 (1978).

[9] P. Hafner and W. H. E. Schwarz, J. Phys. B **11**, 217 (1978).

[10] P. Schwerdtfeger, L. v. Szentpaly, K. Vogel, H. Silberbach, and H. Preuss, J. Chem. Phys. **84**, 1606 (1986).

[11] F. Rosicky, P. Weinberger, and F. Mark, J. Phys. B **9**, 2971 (1976).

[12] J. G. Snijders and E. J. Baerends, Mol. Phys. **36**, 1789 (1978).

[13] G. Hardekopf and J. Sucher, Phys. Rev. A **30**, 703 (1984); **31**, 2020 (1985); (private communication).

[14] J. M. Levy-Leblond, Commun. Math. Phys. **6**, 286 (1967).

[15] M. Kissel-Philipp, Ph.D. Thesis, University of Siegen, 1988.

[16] J. Karwowski and J. Kobus, Chem. Phys. **55**, 361 (1981).

[17] A. Erde'lyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi, *Higher Transcendental Functions* (McGraw-Hill, New York, 1953), Vol 1; F. Mark, E. Ziemniak, and F. Rosicky,

Schriftenreihe des Max-Planck-Institut für Strahlenchemie No. 23, Mülheim, 1985 (unpublished).

[18] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products,* edited by A. Jeffrey (Academic, New York, 1965).

[19] F. Gesztesy, B. Thaller, and H. Grosse, Phys. Lett. B **116**, 155 (1982).

[20] Y. R. Kwon and F. Tabakin, Phys. Rev. C **18**, 932 (1978).

[21] P. Cea, G. Nardulli, and G. Paiano, Phys. Rev. D **28**, 2291 (1983); P. Castorina, P. Cea, G. Nardulli, and G. Paiano, *ibid.* **29**, 2660 (1984).

[22] B. Durand and L. Durand, Phys. Rev. D **28**, 396 (1983); L. J. Nickisch, L. Durand, and B. Durand, *ibid.* **30**, 660 (1984); L. Durand, *ibid.* **32**, 1257 (1985).

[23] J. L. Friar and E. L. Tomusiak, Phys. Rev. C **29**, 1537 (1984).

[24] B. A. Hess, P. Chandra, and R. J. Buenker, Mol. Phys. **52**, 1177 (1984).

[25] F. Papp, Phys. Rep. **136**, 104 (1985).

[26] C. Tzara, Phys. Lett. **111**, 343 (1985).

[27] A. Farazdel and V. H. Smith, Int. J. Quantum Chem. **29**, 311 (1986).

[28] I. W. Herbst, Commun. Math. Phys. **53**, 285 (1977).

[29] I. Daubechies and E. H. Lieb, Commun. Math. Phys. **90**, 497 (1983).

[30] P. Marmier, *Kernphysik I* (Verlag der Fachvereine, Zürich, 1980).