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Numerical solution of the relativistic pair equation

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Correlation has been treated relativistically by solutions of the pair equation, an inhomogeneous differential equation in two dimensions. The equation is solved within the no-(virtual-)pair approximation and is formally correct to order α^2 Ry. Continuum dissolution is rigorously avoided by the use of projection operators. Correlation is treated starting from a suitable choice of a fully relativistic one-particle description of the atom. The solution of the equation involves additional difficulties as compared with the nonrelativistic case, which are discussed. Second-order energies arising from electrostatic and magnetic correlation have been calculated for the $1s^2$ ground state for a series of heliumlike systems ($Z=2-50$). The starting point has been either hydrogenlike wave functions or Dirac-Fock orbitals. Comparison has been made with other methods, showing good, sometimes excellent, agreement, and trends in the isoelectronic series are discussed. By iterative solutions of the exact pair equation a nonperturbative treatment of the two-body part of the static Coulomb interaction is obtained. This procedure has been used for s excitations.

I. INTRODUCTION

Theoretical results are often needed in order to extract interesting physics from experiments. In atomic physics this applies, e.g., to parity-nonconserving phenomena, hyperfine structure, or the physics in highly ionized atoms. To get accurate predictions it is necessary to include also the correlation between the electrons in the calculation. If atoms with large Z values are considered a relativistic treatment is essential also for the correlation.

When nonrelativistic many-body procedures are extended to the relativistic case special care must be taken when performing the infinite sum over excited states, which, implicitly or explicitly, has to be included when second or higher corrections to, e.g., the energy are considered. The Dirac equation provides both positive- and negative-energy solutions and a state of two bound electrons is then formally degenerate with an infinite number of states where one electron is in the negative continuum and the other in the very high positive continuum. In this picture the bound state should then be able to autoionize.[1,2] However, there is an extra boundary condition added to the equation which prevents such transitions; the negative-energy states should be considered as filled under normal conditions. This additional constraint must be kept in mind when dealing with the negative-energy states. As long as only one-particle equations are considered this is no problem; both positive- and negative-energy states will be correctly treated when, e.g., the Dirac-Fock equation is solved. This is connected to the fact that the one-particle Hamiltonian itself defines the meaning of the words positive and negative energy, as discussed in Ref. 3. When, however, real two-body equations are considered it becomes important to be able to distinguish positive- and negative-energy states so that the negative ones could be treated as already occupied. The contribution from the negative-energy states, i.e., from creation of virtual electron-positron pairs, is, however, very tiny and may in many cases be neglected. This is the so-called no-(virtual-)pair approximation. In this approximation the sum over intermediate states is restricted to those with positive energy.

If a basis set consisting of eigenfunctions to the one-particle Hamiltonian in question is available it is no problem to distinguish between states with positive and negative energy and they can both be treated in a correct way, as have been done in a number of works,[4-9] although most calculations stay inside the no-(virtual-)pair approximation. When, instead, correlation is treated by solving inhomogeneous differential equations, pair equations, where the resulting pair function includes only an implicit sum over higher states, this separation of negative-energy states from positive ones becomes more troublesome.

This problem can be solved by the use of projection operators, which project out positive states, but give zero when working on a negative-energy state. To apply projection operators is, however, not a trivial task. Free particle projection operators can be given a closed analytical form and are then possible to use. Such projection operators have been applied in practical calculations.[10,11] However, the use of projection operators not corresponding to the one-particle Hamiltonian actually used in the calculation will, in fact, introduce negative-energy states to the Hamiltonian of interest, rather than remove them as discussed in Ref. 3 and showed in practice in Ref. 10. This can be understood by noting the simple fact that in order to express positive-energy states corresponding to one particular Hamiltonian, in a basis set defined by another Hamiltonian, both positive- and negative-energy states of the latter have to be used. It is therefore important to find projection operators which define states as having positive or negative energy in the presence of a realistic potential, which is at least close to that actually used in the calculation. In particular, it is important to take the singularity at the nucleus into account.

Projection operators of this kind, working in the field of a one-particle potential of free choice, have been set up in Ref. 12 and applied to the relativistic pair equation. The resulting equation is correct to order α^2 Ry and is free from any problems with continuum dissolution. This has been discussed in detail in Ref. 12. A brief review together with preliminary results is given also in Refs. 13 and 14. The details of the projection will not be discussed here; only a short summary is given in Sec. III. In Sec. II the pair equation and the projection operators are presented.

The properties of the pair equation will be discussed in some detail in Sec. IV. To a large extent the equation is treated in the same way as the nonrelativistic pair equation[15] was earlier, but certain operators in the relativistic equation need special care. Results for two-electron systems in the range $Z=2-50$ are given in Sec. V. Some comments on the solution procedure are given in the Appendix.

The procedure developed in the nonrelativistic case, where couplings between different excitations in higher orders are treated self-consistently by iterative solutions of the pair equation, leading to a nonperturbative treatment of the Coulomb interaction, can be applied also in the relativistic case. The difference will only be a non-negligible increase in complexity and computing time. In this work, however, mainly the first-order pair equation has been solved, giving second-order correlation energies for the electrostatic and the magnetic interactions. In the latter case the pair equation is still solved with only electrostatic terms included and the magnetic interaction is applied as a perturbation giving one order in each interaction. It is also possible to set up a pair equation for the Breit interaction,[12] but this more complete approach will be left for future investigations. Retardation terms are not considered in this work. For $1s^2 \rightarrow s^2$ excitations the pair equation has been solved to all orders, indicating the possibility of a nonperturbative procedure.

II. THE EQUATION FOR A TWO-ELECTRON SYSTEM

An "exact" two-particle wave function [inside the framework of the no-(virtual-)pair approximation] for a heliumlike system satisfies the equation

$$H\Psi(1,2)=[h_0(1)+h_0(2)+V_{12}]\Psi(1,2)=E\Psi(1,2)\,, \tag{2.1}$$

where a suitable decomposition of H has been done and h_0 denotes, e.g., the relativistic hydrogenlike Hamiltonian, which is known to satisfy

$$h_0\psi_0=\varepsilon_0\psi_0\,. \tag{2.2}$$

$\Psi(1,2)$ can now be divided into an antisymmetrized product of one-particle wave functions ψ_0 and a deviation $\rho(1,2)$ from that first approximation. The so-called pair function ρ is required to be orthogonal to ψ_0, i.e., intermediate normalization is used. We can then write

$$\Psi(1,2)=\{\psi_a(1)\psi_b(2)+\rho(1,2)\}\,, \tag{2.3}$$

where the curly brackets denote antisymmetrization.

Equation (2.1) now gives

$$\begin{aligned}H\Psi(1,2)&=[h_0(1)+h_0(2)+V_{12}]\{\psi_a(1)\psi_b(2)+\rho(1,2)\}\\&=(\varepsilon_a+\varepsilon_b+\Delta E)\{\psi_a(1)\psi_b(2)+\rho(1,2)\}\end{aligned} \tag{2.4}$$

where

$$\Delta E=\langle\{\psi_a(1)\psi_b(2)\}\mid V_{12}\mid\{\psi_a(1)\psi_b(2)+\rho(1,2)\}\rangle$$

as can be seen by taking the scalar product of (2.4) with $\langle\{\psi_a(1)\psi_b(2)\}\mid$ and making use of the intermediate normalization as well as of (2.2). We will, however, choose to work with non-(anti)symmetrized wave functions and write then

$$\begin{aligned}&[\varepsilon_1+\varepsilon_2-h_0(1)-h_0(2)]\rho_{ab}(1,2)\\&\quad=V_{12}\mid\psi_a(1)\psi_b(2)+\rho_{ab}(1,2)\rangle-\sum_{cd=ab,ba}\mid\psi_c(1)\psi_d(2)+\rho_{cd}(1,2)\rangle\langle\psi_c(1)\psi_d(2)\mid V_{12}\mid\psi_a(1)\psi_b(2)+\rho_{ab}(1,2)\rangle\,.\end{aligned} \tag{2.5}$$

By keeping only first-order terms, a lowest-order pair equation is obtained as follows:

$$[\varepsilon_1+\varepsilon_2-h_0(1)-h_0(2)]\rho_0(1,2)=V_{12}\mid\psi_a(1)\psi_b(2)\rangle-\sum_{cd=ab,ba}\mid\psi_c(1)\psi_d(2)\rangle\langle\psi_c(1)\psi_d(2)\mid V_{12}\mid\psi_a(1)\psi_b(2)\rangle\,. \tag{2.6}$$

Equation (2.6) is a pure two-particle equation; the generalization to the many-body situation is in lowest order given by [see Eq. (13.102) in Ref. 16]

$$\begin{aligned}[\varepsilon_a+\varepsilon_b-h_0(1)-h_0(2)]\rho_{ab}(1,2)&=\sum_{rs}^{\text{exc}}\mid rs\rangle\langle rs\mid V_{12}\mid ab\rangle\\&=V_{12}\mid ab\rangle-\text{orthogonality terms}\,.\end{aligned} \tag{2.7}$$

Here the closure relation has been used to remove the infinite sum over excited states and the orthogonalization is performed to all occupied states. Both (2.6) and the last expression of (2.7) contain thus an implicit summation over nonoccupied states. Since (2.7) is an equation for the many-body situation, h_0 denotes here a one-particle Hamiltonian suitable for that case, e.g., the Dirac-Fock Hamiltonian.

A. Projection operators

The nonrelativistic pair equation, obtained by using $h_0 = h_{\mathrm{Sch}}$, the Schrödinger single-electron Hamiltonian, has been used for a long time to treat correlation effects in connection with, e.g., energies,[15,17,18] hyperfine structure,[19] and isotope shifts,[17,20] mostly for light elements ($Z \leq 37$). The relativistic counterpart is obtained by using $h_0 = h_D$, the Dirac Hamiltonian. V_{12} represents the electrostatic interaction $1/r_{12}$ (or in a more complete approach the full Breit-Coulomb interaction[12]). When starting from hydrogenlike orbitals both single and double excitations caused by $1/r_{12}$ will be included in the pair function. If, instead, Dirac-Fock orbitals are chosen as the first-order approximation only double excitations will be included in first order since the one-body part of $1/r_{12}$ is already taken into account in the orbitals. In order to restrict the inclusion of intermediate states to those with positive energy, V_{12} must in the relativistic case be surrounded with projection operators λ_+. The implicit summation over excited states will otherwise automatically include even negative-energy states since only a summation over *all* states fulfills the closure relation. We write then

$$[\varepsilon_a + \varepsilon_b - h_D(1) - h_D(2)]\rho(1,2) = \lambda(1)_+ \lambda(2)_+ \frac{1}{r_{12}} \left| ab \right\rangle - \sum_{cd}^{\mathrm{occ}} \left| cd \right\rangle \left\langle cd \left| \frac{1}{r_{12}} \right| ab \right\rangle . \tag{2.8}$$

This equation consist of four coupled first-order differential equations and both $\rho(1,2)$ and the right-hand side of (2.8) are spinors consisting of four spatial components. The projection operator is written

$$\lambda_+ = \begin{bmatrix} \Omega_+^2 & \Omega_+^2 R_+^\dagger \\ R_+ \Omega_+^2 & R_+ \Omega_+^2 R_+^\dagger \end{bmatrix} , \tag{2.9}$$

where R_+ is given by the implicit relation

$$R_+ = \frac{1}{2mc^2 - V}[c\sigma\cdot\mathbf{p} - R_+ V - R_+ (c\sigma\cdot\mathbf{p}) R_+] \tag{2.10}$$

and

$$\Omega_+^2 = (1 + R_+^\dagger R_+)^{-1} . \tag{2.11}$$

These equations are given and discussed in more detail in Refs. 12 and 21. The operator R_+ has the property of giving the small component G when operating on the large component F of a solution to the Dirac equation with positive energy. F and G denote two-component spinors of Pauli type. The R_+ operator, in the following written simply as R, cannot be expressed in closed form, but keeping only the first, dominating term gives

$$R_0 = \frac{1}{2mc} \frac{1}{1 - V/2mc^2} \sigma\cdot\mathbf{p} , \tag{2.12}$$

which is a good approximation at least for neutral and medium ionized systems for most elements as investigated in Ref. 13. (For the outermost part of the wave function the approximation affects the result of R with about 4% for the 1*s* state of hydrogenlike cesium. Closer to the nucleus where the potential is very large and negative the effect of the approximation is much smaller.)

III. THE RELATIVISTIC PAIR EQUATION

Equation (2.8) is the starting point for the calculation. The projection operators on the right-hand side assure that the two-body potential is not mixing in any erroneous states. However, as can be seen from the left-hand side, (2.8) has, in addition to the solution corresponding to the given right-hand side, an infinite number of homogeneous solutions. These can be avoided by making use of the R operator (2.10) as will be indicated below. Writing (2.8) more explicitly gives

$$\begin{aligned}
&(\varepsilon_a + \varepsilon_b - V_1 - V_2)\rho^{LL} - c(\sigma\cdot\mathbf{p})_1\rho^{SL} - c(\sigma\cdot\mathbf{p})_2\rho^{LS} = \bar{P}^{LL} , \\
&(\varepsilon_a + \varepsilon_b - V_1 - V_2 + 2mc^2)\rho^{LS} - c(\sigma\cdot\mathbf{p})_1\rho^{SS} - c(\sigma\cdot\mathbf{p})_2\rho^{LL} = \bar{P}^{LS} , \\
&(\varepsilon_a + \varepsilon_b - V_1 - V_2 + 2mc^2)\rho^{SL} - c(\sigma\cdot\mathbf{p})_1\rho^{LL} - c(\sigma\cdot\mathbf{p})_2\rho^{SS} = \bar{P}^{SL} , \\
&(\varepsilon_a + \varepsilon_b - V_1 - V_2 + 4mc^2)\rho^{SS} - c(\sigma\cdot\mathbf{p})_1\rho^{LS} - c(\sigma\cdot\mathbf{p})_2\rho^{SL} = \bar{P}^{SS} ,
\end{aligned} \tag{3.1}$$

where $\bar{P}^{LL}, \bar{P}^{LS}, \bar{P}^{SL}, \bar{P}^{SS}$ denote the four components of the projected right-hand side.

This set of equations can easily be transformed into the following two coupled second-order differential equations by using the expressions for ρ^{LS} and ρ^{SL} from the second and third equation in the first and fourth equation, giving a large-large and a small-small equation (from here on we have used atomic units $m = 1, e = 1, 4\pi\varepsilon_0 = 1, \hbar = 1, 1/c = \alpha$):

$$\{\varepsilon_a + \varepsilon_b - V_1 - V_2 - \tfrac{1}{2}[(\sigma\cdot\mathbf{p})_1 B_{ab} (\sigma\cdot\mathbf{p})_1 + (\sigma\cdot\mathbf{p})_2 B_{ab} (\sigma\cdot\mathbf{p})_2]\}\rho^{LL} = \bar{P}^{LL} + \tilde{R}_1^\dagger \bar{P}^{SL} + \tilde{R}_2^\dagger \bar{P}^{LS} + \tfrac{1}{2}[(\sigma\cdot\mathbf{p})_1 B_{ab} (\sigma\cdot\mathbf{p})_2 + (\sigma\cdot\mathbf{p})_2 B_{ab} (\sigma\cdot\mathbf{p})_1]\rho^{SS} , \tag{3.2}$$

$$\rho^{SS} + \frac{\alpha^2}{4}\{\varepsilon_a + \varepsilon_b - V_1 - V_2 - \tfrac{1}{2}[(\sigma\cdot\mathbf{p})_1 B_{ab} (\sigma\cdot\mathbf{p})_1 + (\sigma\cdot\mathbf{p})_2 B_{ab} (\sigma\cdot\mathbf{p})_2]\}\rho^{SS} = \frac{\alpha^2}{4}\frac{1}{2}[(\sigma\cdot\mathbf{p})_1 B_{ab} (\sigma\cdot\mathbf{p})_2 + (\sigma\cdot\mathbf{p})_2 B_{ab} (\sigma\cdot\mathbf{p})_1]\rho^{LL} + \frac{\alpha^2}{4}(\bar{P}^{SS} + \tilde{R}_2^\dagger \bar{P}^{SL} + \tilde{R}_1^\dagger \bar{P}^{LS}) . \tag{3.3}$$

For convenience we have introduced

$$B_{ab}=[1+(\varepsilon_a+\varepsilon_b-V_1-V_2)/2mc^2]^{-1}\ , \tag{3.4}$$

$$\tilde{R}=(\varepsilon_a+\varepsilon_b-V_1-V_2+2mc^2)^{-1}c\sigma\cdot\mathbf{p}=\frac{\alpha}{2}B_{ab}\sigma\cdot\mathbf{p}\ .$$

$\tilde{R}$ is to order α^2 equal to R, and also to R_0, the first term in the expression for R, given in (2.12).

The projected components of the right-hand side are easily obtained from the unprojected right-hand side by using the projection operator (2.9). As is shown in detail in Ref. 12 the effect of the projection operator, when dealing with a diagonal operator such as the static Coulomb interaction, will not enter until order α^4 Ry. In this order also effects arising from creation of virtual electron-positive pairs will enter and for the purpose of getting the correlation correct to α^2 Ry it is then justified to use the unprojected right-hand side.

The coupled system of (3.2) and (3.3) will, of course, have the same homogeneous solutions as (2.8). As discussed in Ref. 12 these solutions can be avoided by invoking the R operator and using the expression

$$\rho^{SS}=R_1R_2\rho^{LL}\approx R_0(1)R_0(2)\rho^{LL} \tag{3.5}$$

rather then the solution from Eq. (3.3) for ρ^{SS} on the right-hand side of (3.2). As discussed in Sec. II, the R operator gives the small component when working on the large component of a positive-energy state. A possible homogeneous solution to (2.8) will consist of one electron in the negative continuum, $\varepsilon=-2mc^2$, and one in the very high positive continuum, $\varepsilon=2mc^2$. For such a state (3.5) will not be a good approximation at all. Instead of ρ^{SS} the relation will give a result of the order of $\sim\alpha^2\rho^{SS}$ and since the ρ^{SS} term is crucial for the cancellation of the terms on the left-hand side, producing the homogeneous solutions, these undesired solutions will no longer be possible. In this way also a simplified solution procedure is obtained, since only the large-large equation (3.2) now has to be solved and the other three components could be given as

$$\begin{aligned}\rho^{LS}&=R_0(2)\rho^{LL}+O(\alpha^3)\ ,\\ \rho^{SL}&=R_0(1)\rho^{LL}+O(\alpha^3)\ ,\\ \rho^{SS}&=R_0(1)R_0(2)\rho^{LL}+O(\alpha^4)\ .\end{aligned} \tag{3.6}$$

When calculating matrix elements using (3.6) the approximation affects the result for both diagonal and off-diagonal operators in order α^4 Ry.

IV. THE LARGE-LARGE PAIR EQUATION

A. The radial large-large equation

Since the right-hand side of (3.2) is easily decomposed in radial and angular parts using

$$\frac{1}{r_{12}}=\sum_k(-1)^qC_q^k(1)C_{-q}^k(2)\frac{r_<^k}{r_>^{k+1}}\ ,$$

where

$$C_q^k(i)=[4\pi/(2k+1)]^{1/2}Y_{kq}(\theta_i,\phi_i)$$

are the Racah tensors, the pair function can be expressed as

$$\rho_{ab}=\sum_{k,\kappa_r,\kappa_s}\ \sum_{m_r,m_s}\rho(k,ab\rightarrow\kappa_r\kappa_s)G^k(r,s,a,b)\ ,$$

where

$$\rho(k,\,ab\rightarrow\kappa_r\kappa_s)$$

$$=\frac{1}{r_1r_2}\begin{bmatrix}\rho^{LL}(r_1,r_2)(\mathcal{X}_1)_{\kappa_1m_1}(\mathcal{X}_2)_{\kappa_2m_2}\\ i\rho^{LS}(r_1,r_2)(\mathcal{X}_1)_{\kappa_1m_1}(\mathcal{X}_2)_{-\kappa_2m_2}\\ i\rho^{SL}(r_1,r_2)(\mathcal{X}_1)_{-\kappa_1m_1}(\mathcal{X}_2)_{\kappa_2m_2}\\ -\rho^{SS}(r_1,r_2)(\mathcal{X}_1)_{-\kappa_1m_1}(\mathcal{X}_2)_{-\kappa_2m_2}\end{bmatrix} \tag{4.1}$$

and

$$\kappa=\mp(j+\tfrac{1}{2}),\quad j=l\pm\tfrac{1}{2}\ .$$

G is represented by the angular momentum graph in Fig. 1 and can be evaluated by standard techniques.[16] Here $\mathcal{X}$ is a vector-coupled function of a spherical harmonic and a spin function. $\mathcal{X}$ is given in the ls convention $\rho=|\,lsjm\,\rangle$. We now let ρ represent the radial function of the right-hand side of (4.1). After working out the expressions $\sigma\cdot\mathbf{p}B_{ab}\sigma\cdot\mathbf{p}$, using the operator identity, $(\sigma\cdot\mathbf{A})(\sigma\cdot\mathbf{B})=\mathbf{A}\cdot\mathbf{B}+i\sigma\cdot(\mathbf{A}\times\mathbf{B})$, and dividing both sides with B_{ab}, given in (3.4), the large-large pair equation, (3.2), can be written

$$\begin{aligned}&(\varepsilon_a+\varepsilon_b-V_1-V_2)\rho^{LL}+\frac{1}{2}\left[\frac{\partial^2}{\partial r_1^2}-\frac{\kappa_1}{r_1^2}(\kappa_1+1)+\frac{\partial^2}{\partial r_2^2}-\frac{\kappa_2}{r_2^2}(\kappa_2+1)\right]\rho^{LL}+\frac{\alpha^2}{2}(\varepsilon_a+\varepsilon_b-V_1-V_2)^2\rho^{LL}\\ &\quad+\frac{\alpha^2}{4}B_{ab}\left[\frac{\partial V_1}{\partial r_1}\left[\frac{\partial}{\partial r_1}-\frac{1}{r_1}\right]+\frac{\partial V_1}{\partial r_1}\frac{1}{r_1}(\kappa_1+1)+\frac{\partial V_2}{\partial r_2}\left[\frac{\partial}{\partial r_2}-\frac{1}{r_2}\right]+\frac{\partial V_2}{\partial r_2}\frac{1}{r_2}(\kappa_2+1)\right]\rho^{LL}\\ &\quad-B_{ab}^{-1}\tfrac{1}{2}[(\sigma\cdot\mathbf{p})_1B_{ab}(\sigma\cdot\mathbf{p})_2+(\sigma\cdot\mathbf{p})_2B_{ab}(\sigma\cdot\mathbf{p})_1]R_0(1)R_0(2)\rho^{LL}\\ &\qquad=B_{ab}^{-1}\left[P^{LL}-\frac{\alpha}{2}\left[\frac{\partial}{\partial r_1}-\frac{\kappa_1}{r_1}\right]B_{ab}P^{SL}-\frac{\alpha}{2}\left[\frac{\partial}{\partial r_2}-\frac{\kappa_2}{r_2}\right]B_{ab}P^{LS}\right]+O(\alpha^4)\ .\end{aligned} \tag{4.2}$$

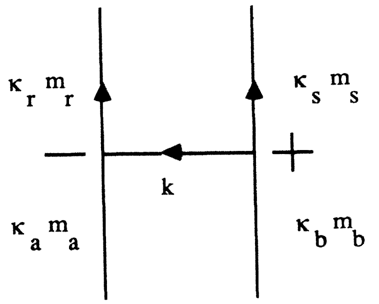

FIG. 1. Angular momentum graph for $G^k(r,s,a,b)$. Each vertex represent a 3-j symbol and the sign at the vertex tells if the angular momenta are to be read in positive or negative direction. Summation is implied over m values of internal lines. For further details see Ref. 16.

The last two terms on the left-hand side are obtained from the last two terms on the right-hand side of (3.2) by the use of (3.5). The equation resembles the nonrelativistic pair equation. Written in this form the first line, except the last term, is identical to the nonrelativistic left-hand side. In addition there are the α^2 terms, which will vanish in the nonrelativistic limit. The first and third term on the second line of the left-hand side of (4.2) are terms corresponding to the Darwin term in the Pauli approximation. The second and the fourth terms on the same line are the well-known spin-orbit interaction. On the right-hand side, terms due to the spin-orbit coupling for one electron moving in the field from the other electron are recognized,

$$\begin{aligned}\frac{\alpha}{2}\left[\frac{\partial}{\partial r_1}-\frac{\kappa_1}{r_1}\right]P^{SL}&=\frac{\alpha}{2}(\boldsymbol{\sigma}\cdot\mathbf{p})_1\frac{1}{r_{12}}\,|\,G_aF_b\,\rangle\\&=\frac{\alpha^2}{4}(\boldsymbol{\sigma}\cdot\mathbf{p})_1\frac{1}{r_{12}}(\boldsymbol{\sigma}\cdot\mathbf{p})_1\,|\,F_aF_b\,\rangle+O(\alpha^4)\\&=\frac{\alpha^2}{4}\left[\mathbf{p}\frac{1}{r_{12}}\mathbf{p}+i\boldsymbol{\sigma}\cdot\left[\mathbf{p}\frac{1}{r_{12}}\times\mathbf{p}\right]\right]\,|\,F_aF_b\,\rangle+O(\alpha^4)\,,\end{aligned}\tag{4.3}$$

where the first term includes a two-particle Darwin-like term, similar to the Darwin-like term due to the one-particle potential on the left-hand side. The second term is the spin-orbit term just mentioned. [In (4.3) the orthogonalization term in (2.8), implicitly present in P^{SL}, has been omitted for simplicity.]

It may be noted that the second and third terms on the right-hand side of (4.2), originating from the large-small and small-large right-hand side, include derivatives of a cusp, since there is a cusp in $r_<^k/r_>^{k+1}$ for $r_1=r_2$. The derivatives are then together forming an even steeper cusp. In order not to lose numerical accuracy these derivatives should be carried out with some care.

B. Comparison with the Pauli approximation

Even if the relativistic terms in (4.2) are slightly similar to the operators in the Pauli approximation (see p. 181 in Ref. 22), the only approximation made here is when the approximate R operator R_0 [see (2.12)] is used to obtain ρ^{SS},ρ^{LS} and ρ^{SL} from ρ^{LL}, and when the projection operators are applied. R_0 is also a better approximation of R than the corresponding "Pauli form,"[23] since the denominator in (2.12), which includes the nuclear potential, ensures the inclusion of the dominating parts of relativistic corrections of orders higher than $(\alpha Z)^2$ Ry as discussed in Ref. 13. That Eq. (4.2) is not equivalent to a Pauli approximation is in particular manifested by the absence of δ functions and by the less divergent form of all the relativistic operators when smoothed by the B functions close to the nucleus. Fully relativistic one-particle orbitals are also used as the lowest approximation, which means that the electron-nucleus interaction and the part of the electron-electron interaction which can be described by single excitations are treated without approximations (within the framework of the Dirac equation). The correct treatment of the electron-nucleus interaction is especially important since terms of high order in α, accompanied by the nuclear potential, are not necessarily "small" close to the nucleus due to the singularity of the nuclear field. The difference between the results obtained with (4.2) and using the Pauli approximation can be viewed in Fig. 2.

C. The existence of a $\mathbf{p}_1^2\mathbf{p}_2^2$ term

The α^2 term on the first line of (4.2) and also the terms on the last line of the left-hand side take care of the kinetic correction in the relativistic case and have thus an effect similar to that of the $\mathbf{p}^4$ term in the Pauli approximation. A closer investigation of the terms on the last line of the left-hand side shows that these are not without complications,

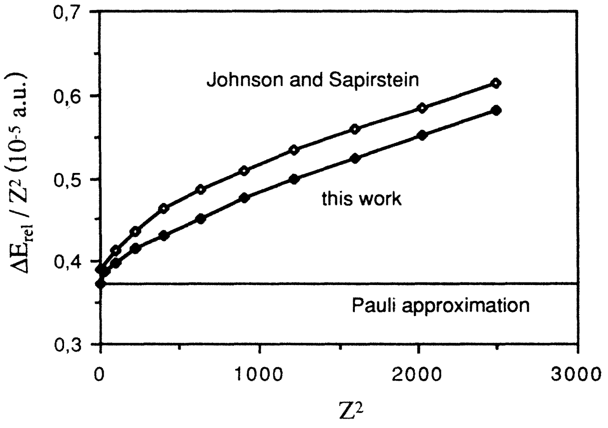

FIG. 2. Relativistic contributions to the correlation energy, obtained with hydrogenlike orbitals for $Z=2$–50 (see Table II), divided by Z^2 and plotted against Z^2. A comparison is here made between the calculation performed by Johnson and Sapirstein (Ref. 9) and this work. The result obtained with the Pauli approximation, i.e., including only α^2Z^2 terms, such as the value extracted from Pekeris (Ref. 24), is given by the line parallel with the x axis. The curves obtained in this work and in the work by Johnson and Sapirstein should both intersect the y axis at the Pauli value. The slope of the curves is, for small Z, given by α^4Z^4 terms and the bending is the result of terms of higher orders of αZ.

$$
\begin{aligned}
&B_{ab}^{-1}\tfrac{1}{2}[(\sigma\cdot\mathbf{p})_1B_{ab}(\sigma\cdot\mathbf{p})_2+(\sigma\cdot\mathbf{p})_2B_{ab}(\sigma\cdot\mathbf{p})_1]R_0(1)R_0(2)\rho^{LL}\\
&\quad=\alpha^2B_{ab}^{-1}\tfrac{1}{8}[(\sigma\cdot\mathbf{p})_1B_{ab}(\sigma\cdot\mathbf{p})_2+(\sigma\cdot\mathbf{p})_2B_{ab}(\sigma\cdot\mathbf{p})_1]B_1B_2(\sigma\cdot\mathbf{p})_1(\sigma\cdot\mathbf{p})_2\rho^{LL}\\
&\quad=\Bigg[\frac{\alpha^2}{4}B_1B_2\left[\frac{\partial^2}{\partial r_1^2}-\frac{\kappa_1}{r_1^2}(\kappa_1+1)\right]\left[\frac{\partial^2}{\partial r_2^2}-\frac{\kappa_2}{r_2^2}(\kappa_2+1)\right]\\
&\qquad+\frac{\alpha^2}{8}B_2\{B_1B_{ab}^{-1}[(\sigma\cdot\mathbf{p})_1,B_{ab}]+2[(\sigma\cdot\mathbf{p})_1,B_1]\}(\sigma\cdot\mathbf{p})_1\left[\frac{\partial^2}{\partial r_2^2}-\frac{\kappa_2}{r_2^2}(\kappa_2+1)\right]\\
&\qquad+\frac{\alpha^2}{8}B_1\{B_2B_{ab}^{-1}[(\sigma\cdot\mathbf{p})_2,B_{ab}]+2[(\sigma\cdot\mathbf{p})_2,B_2]\}(\sigma\cdot\mathbf{p})_2\left[\frac{\partial^2}{\partial r_1^2}-\frac{\kappa_1}{r_1^2}(\kappa_1+1)\right]+O(\alpha^6)\Bigg]\rho^{LL}\,, \qquad (4.4)
\end{aligned}
$$

where

$$B_i=\left[1+\frac{\alpha^2}{2}V_i\right]^{-1} . \qquad (4.5)$$

The commutators with B_i or B_{ab} add an extra factor α^2. We now have, in addition to the second-order derivatives, already present at the left-hand side of (4.2), a cross-derivative term originating from $\mathbf{p}_1^2\mathbf{p}_2^2$. It may be tempting to try to neglect this term in the first approximation and then solve the equation again with the cross-derivative term on the right-hand side applied to the previously obtained solution. That is, however, not a workable method. The right-hand side has a cusp on the diagonal, $r_1=r_2$, and the leading derivative will have to reproduce this behavior. Neglecting the cross-derivative term means that the ordinary second-order derivatives on the pair function will represent a cusp and any attempt to perform a second derivative once more will lead to a δ function. If, however, the equation is really solved with this cross-derivative term on the left-hand side, the ordinary second derivative and the cross-derivative term together will represent the cusp and no δ function will show up. In the preliminary calculations[13,14] an approximation was done for this term and the remaining part was treated as a first-order perturbation. The whole term was then included in the second-order energy, but a part of it was missing in the construction of the wave function. In this work, however, the whole term has been included in the solution of the pair equation.

To solve the equation, the solution procedure developed for the nonrelativistic pair equation[15] was applied, although some nontrivial modifications were done to include the cross-derivative term discussed above. The differences compared to the nonrelativistic treatment are described in the Appendix.

V. RESULTS

A. Hydrogenlike orbitals

When starting from hydrogenlike orbitals the zeroth-order Hamiltonian contains no interaction between the electrons, and the pair equation (2.6) is used with V_{12} representing the full interaction $1/r_{12}$. In first order the pair function will consist of the first ladder diagram on the right-hand side in Fig. 3.

If we instead solve the all-order pair equation (2.5), then all the diagrams in Fig. 3 will be included. This solution can be obtained iteratively by adding terms involving the previously obtained solution to the right-hand side and solving again until convergence. In this work this is only done for s excitations, which means that all the intermediate states are restricted to s states, while in a complete calculation all partial waves should be allowed to mix in higher orders.

Table I shows the second-order contributions from different excitations for $Z=2$ and $Z=10$. For $Z=2$ the l-extrapolated result for the electrostatic correlation agrees well with both the second-order values from Johnson and Sapirstein,[9] obtained with a relativistic (rel) [no-(virtual)-pair] method, and with the result from Pekeris.[24] Pekeris's values are obtained using Hylleraas-type "exact" wave functions for the nonrelativistic (nrel) part and the contribution from the Breit-Coulomb operators in the Pauli approximation (p. 181 in Ref. 22) are then added as a first-order perturbation. Since this is done for $Z=1-10$, the values can be fitted to a Z-expansion formula[9,25,26] in order to extract the second-order relativistic energy. The relativistic corrections thus obtained are the contributions from the Breit-Pauli operators[27,28] which depend linearly on Z^2.

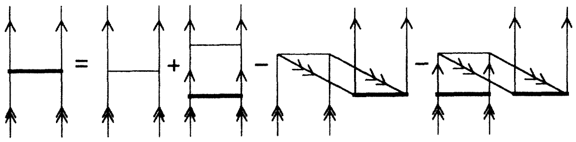

FIG. 3. Diagrammatic representation of the all-order pair equation (2.5). A line with double arrows represents a valence orbital and lines with single arrows excited orbitals. The horizontal line represents the Coulomb interaction. The pair function ρ_{ab} is represented by the diagram on the left-hand side. The first-order pair function is given by the first diagram on the right-hand side.

The relativistic corrections to the second-order energy has the following form:

$$\Delta E_{\text{rel}} = a(\alpha Z)^2 + b(\alpha Z)^4 + \cdots \tag{5.1}$$

and only the first term in (5.1) can be obtained from a calculation based on the Pauli approximation. Although the pair equation (4.2) is only rigorously correct to order $(\alpha Z)^2$ Ry it is not a Pauli approximation and it should be emphasized that a large part of higher-order relativistic corrections are included as discussed in Sec. IV B (see also Fig. 2).

For low Z the relativistic correction obtained from Pekeris, the first term in (5.1), should be very accurate but already for $Z=10$ it may be important to use the proper relativistic one-particle orbitals when the Coulomb interaction is evaluated. This is probably the reason why both our calculation and the work by Johnson and Sapirstein show a larger relativistic shift than that obtained by Pekeris. This difference is enlarged for higher Z as seen in Fig. 2.

For $1s^2 \rightarrow s^2$ excitations also the all-order result is given in Table I, indicating the size of the relativistic corrections in higher orders. It is seen that higher-order contributions reduce the relativistic shift. Since relativistic effects from s excitations are lowering the energy in

TABLE I. Second-order correlation energies, obtained with hydrogenlike orbitals for $Z=2$ and 10, given in units of 10^{-6} a.u. The values in this table are obtained after extrapolation using three grid sizes.

	$Z=2$			$Z=10$	
	Electrostatic		Magnetic	Electrostatic	Magnetic
	rel	rel-nrel[a]			
Second-order					
$1s^2$ to s^2	$-125\,356.0$	-22.3	-68.3	$-125\,896$	-1706
$p_{1/2}^2$	-8828.3	3.4	-22.0	-8747	-542
$p_{3/2}^2$	$-17\,664.1$	-0.7	-23.6	$-17\,681$	-587
$d_{3/2}^2$	-1561.0	1.4	-6.3	-1529	-151
$d_{5/2}^2$	-2343.5	0.1	-5.1	-2342	-125
$f_{5/2}^2$	-461.2	0.6	-2.9	-446	-69
$f_{7/2}^2$	-615.7	0.1	-2.4	-613	-57
$g_{7/2}^2$	-180.1	0.4	-1.7	-172	-39
$g_{9/2}^2$	-225.5	0.1	-1.4	-223	-33
$h_{9/2}^2$	-83.8	0.2	-1.1	-79	-24
$h_{11/2}^2$	-100.8	0.1	-0.9	-99	-21
$i_{11/2}^2$	-44.0	0.1	-0.8	-41	-16
$i_{13/2}^2$	-51.5	0.1	-0.7	-50	-15
$j_{13/2}^2$	-25.2	0.1	-0.6	-23	-12
$j_{15/2}^2$	-28.9	0.1	-0.5	-28	-11
$k_{15/2}^2$	-15.5	0.1	-0.4	-14	-9
$k_{17/2}^2$	-17.5	<0.1	-0.4	-17	-8
$l_{17/2}^2$	-10.0	0.1	-0.4	-9	-7
$l_{19/2}^2$	-11.2	<0.1	-0.3	-10	-6
$m_{19/2}^2$	-6.8	<0.1	-0.3		
$m_{21/2}^2$	-7.4	<0.1	-0.3		
Total	$-157\,637.7$		-140.4	$-158\,015$	-3436
Extrapolation	$-157\,681$		$-146.$	$-158\,065$	-3531
[b]	$-157\,681.3$			$-158\,038$	
[c]	$-157\,681.5$			$-158\,083$	
E_{rel}-E_{nrel}	-15			-402	
[b]	-14.9			-372	
All order					
$1s^2$ to s^2	$-129\,049.5$		-54.7	$-126\,441$	-1615
Contributions from higher orders					
$1s^2$ to s^2	-3693.5		13.6	$-545.$	91
E_{rel}-E_{nrel}	1.4			9	

[a] The comparison here is done with the nonrelativistic values obtained by solving the nonrelativistic pair equation using the same grid size and extrapolation procedure, which gives $-157\,666 \times 10^{-6}$ a.u.; an "exact" second-order nonrelativistic value should be $-157\,666.4 \times 10^{-6}$ a.u. (Refs. 29 and 30).

[b] Pekeris, "exact" nonrelativistic wave functions, relativistic corrections added as a first-order perturbation (Ref. 24). The second-order result is extracted by fitting the result of Pekeris ($Z=1$–10) to a Z expansion.

[c] Johnson and Sapirstein, piecewise polynomial method (Ref. 9).

second order, while contributions from higher partial waves go in the opposite direction, it is possible that the mixture between different partial waves in higher orders will change the behavior of the relativistic corrections from these orders considerably.

Magnetic correlation is also given in Table I. These values are obtained by the use of pair functions to calculate the so-called Gaunt term[31] from the Breit interaction,[32]

$$-\sum_{i<j}\frac{\alpha_i\cdot\alpha_j}{r_{ij}},$$

but neglecting the retardation term, which is also of order α^2 Ry but has been found to be an order of magnitude smaller.[33] The second-order magnetic results in Table I are one order in electrostatic and one order in magnetic interaction, while the all-order result is of all orders in Coulomb interaction but still only one order in the magnetic part. The diagrams included are illustrated in Figs. 4(b)–4(d). It is not possible to separate the magnetic and retardation terms, given together in Ref. 28, from the results given by Pekeris.[24] However, the second-order magnetic interaction given in Table I agrees within a few percent with unpublished results from Johnson and Sapirstein.[34]

Table II shows the total second-order energies for $Z=2-50$. For $Z=2-30$ l values up to $l=9$ were included and the result was extrapolated. The extrapolation affects the results with three to four units in the last figure. For $Z=35-50$, l values up to $l=5$ were included and the extrapolation accounts for 10–13 units in the last digit, with a possible uncertainty of one to two units. For higher Z, larger than 20, our values show a deviation from the result of Johnson and Sapirstein[9] by 6–8 % of the *relativistic corrections.* A closer investigation of this discrepancy is shown in Fig. 2, where the relativistic corrections divided with Z^2 are plotted against Z^2. A pure α^2Z^2 contribution, the first term in (5.1), as obtained when applying the Breit-Pauli operators in a second-order nonrelativistic calculation, e.g., the values extracted from Pekeris's calculations, should thus only give a straight line parallel to the x axis. α^4Z^4 Ry effects give a straight line, not parallel to the x axis, which cuts the y-axis at the Breit-Pauli value. The actual shape of the curves is the result of terms of order α^4Z^4 and beyond. Only the very first part of the curves can be explained by pure α^4Z^4 terms. We see that the curve from the present work appears to be shifted parallel compared to the curve from Johnson and Sapirstein. This indicates that the difference lies in order α^2Z^2 Ry and could perhaps be sought in differences in numerical treatment. The corrections beyond α^2Z^2 Ry, extracted from the two calculations, agree rather well; the two curves have similar slopes, in spite of the fact that the correlation in this order is not treated in the same way. Both the calculations are correct to order α^2Z^2 Ry and neglect many terms in α^4Z^4 Ry and beyond, e.g., all terms arising from excitations of virtual electron-positron pairs caused by the electronic potential. In the present work additional approximations in order α^4Z^4 Ry are done when applying the R operator, as discussed in Secs. III and IV B. However, these approximations are only affecting the intermediate states and the largest corrections in order α^4Z^4 Ry, present in a no-(virtual-)pair calculation, probably arise from the one-particle energies for the initial state, used in the energy denominator, and from the initial-state wave function. Those are, in both the calculations, the proper relativistic one-particle ones. This is presumably the reason for the closeness of the two slopes.

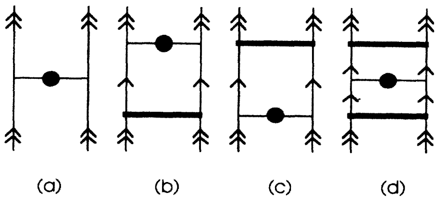

FIG. 4. The last three diagrams, (b)–(d), represent the contribution to the correlation energy included when the magnetic interaction is evaluated with pair functions iterated to all orders. The line with a dot represents the magnetic interaction. Diagram (a) is simply representing the first-order magnetic contribution.

B. Dirac-Fock orbitals

1. *Electrostatic correlation*

When starting from Dirac-Fock orbitals, all single-particle corrections due to $1/r_{12}$ are already taken care of in the zeroth-order wave functions and only real correlation is treated in the perturbation expansion. Table III shows the lowest excitations together with the total result, including up to $l=4$, for $Z=2-50$. For the first Z values the nonrelativistic behavior, $(a+b/Z)$, dominates, as also shown in Figs. 5 and 6. Above $Z=15$ it is, however, seen how the relativistic correction arising from $1s^2\rightarrow s^2$ excitations (Fig. 5) increase the absolute value of the energy, while the total effect from the other angular contributions goes in the opposite direc-

TABLE II. Second-order correlation energies, obtained with hydrogenlike orbitals for $Z=2-50$, given in units of 10^{-5} a.u., all contributions are given with opposite sign.

	Electrostatic correlation		Magnetic correlation
Z	This work[a]	Johnson and Sapirstein[b]	This work[a]
	15 766.6[c]		
2	15 768.1	15 768.1	14.6
5	15 777	15 776	90
10	15 807	15 808	353
15	15 860	15 865	778
20	15 940	15 952	1354
25	16 049	16 070	2074
30	16 195	16 225	2931
35	16 377	16 420	3928
40	16 604	16 661	5048
45	16 882	16 952	6299
50	17 219	17 301	7682

[a] $Z=2-30$ $l_{\max}=9$ included, the rest of the l sum extrapolated; $Z=35-50$ $l_{\max}=5$ included, the rest of the l sum extrapolated.
[b] Piecewise polynomial method (Ref. 9).
[c] Nonrelativistic value independent of Z.

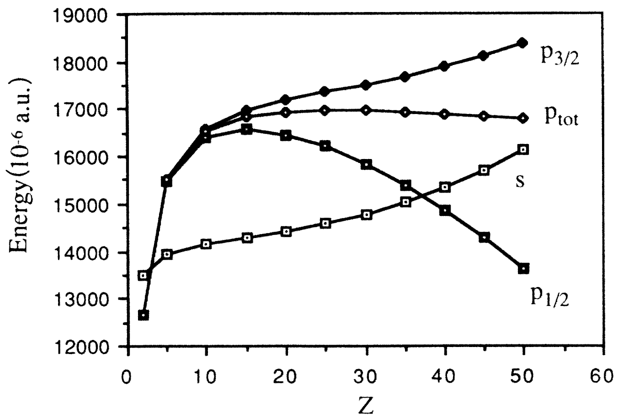

FIG. 5. Contributions to the second-order energy for heliumlike systems from s and p excitations, obtained with Dirac-Fock orbitals. For small Z values the nonrelativistic $(a+b/Z)$ behavior is recognized, but for large Z the relativistic contributions start to dominate the shape of the curves. The contribution from $\kappa<0$ excitations are increasing the absolute value of the energy, while the $\kappa>0$ excitations contribute in an opposite direction, as discussed in Sec. (V B 1). The $p_{1/2}$ curve is scaled with a factor of 2 and the p-total curve is scaled with a factor of $\frac{2}{3}$ in order to get all four curves of comparable size.

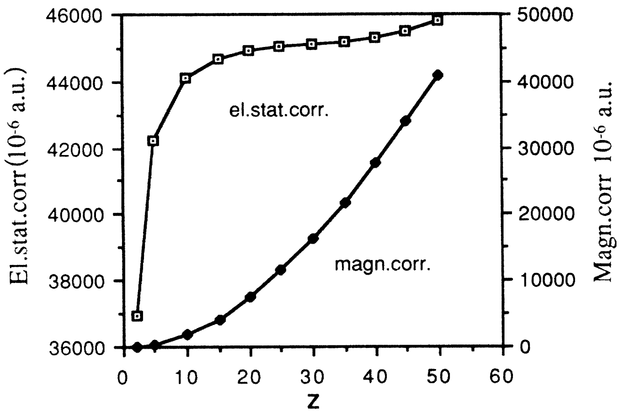

FIG. 6. Second-order electrostatic and magnetic energies for heliumlike systems, obtained with Dirac-Fock orbitals. Partial waves up to $l=4$ were included. The electrostatic energy is for small Z dominated by the nonrelativistic $(a+b/Z)$ behavior. An additional term, which has a Z^2 behavior, is clearly recognizable for large Z and arises from relativistic contributions. Magnetic contributions grow strongly with increasing Z and, for $Z=50$, are of the same size as the total electrostatic contribution.

tion. For negative κ values there is a slight tendency to raise the energy, as for s^2 excitations, but for positive κ values there is a stronger tendency to lower the absolute value of the energy. This may be a surprising effect, since the wave functions with positive κ values are more contracted than the functions with negative κ values and are then expected to have a larger overlap with the $1s^2$ state. However, the four-component structure of the wave functions changes this picture. For a matrix element between states having κ values with opposite sign, as an element between the $1s^2$ state and a $p_{1/2}^2$ state does, the contribution from the large-small and small-large component will work in an opposite direction compared to the large-large component. This is due to the difference in relative sign between the large and small components for states having positive and negative κ values. The contraction of the wave function causes the small component to grow relative to the large component, increasing the contribution from the large-small and small-large matrix elements and thus lowering the total contribution from the excitation in question. In the case when the signs of the κ values are the same for initial and intermediate states the large-small and small-large matrix elements work in the same direction as does the large-large element. This will cause the total contribution to rise if only the growing overlap in the numerator is able to outweigh the also growing denominator, caused by the larger relativistic energy shift in the initial state compared to the intermediate one. As could be seen in Table I (hydrogenlike orbitals) this only happens for s and p states in the case of $Z=2$ or 10, but when Z grows this behavior can also be seen for higher partial waves, e.g., the $d_{5/2}$ excitations are enlarging the relativistic shift above $Z=20$. For Dirac-Fock orbitals (Fig. 5) this turning point is harder to see since the relativistic shift is added to a nonrelativistic contribution which also grows with increasing Z.

The total second-order energy (including up to $l=4$),

TABLE III. Second-order electrostatic correlation obtained with Dirac-Fock orbitals, given in units of 10^{-6} a.u.; all contributions are given with opposite sign.

$1s^2$ to / Z	s^2	$p_{1/2}^2$	$p_{3/2}^2$	$d_{3/2}^2$	$d_{5/2}^2$	total, $l_{\max}=4$
2	13 498	6325	12 654	1277	1916	36 965
5	13 928	7740	15 518	1444	2176	42 213
10	14 160	8202	16 576	1476	2258	44 095
15	14 296	8281	16 961	1455	2285	44 679
20	14 430	8230	17 183	1412	2299	44 922
25	14 588	8105	17 354	1353	2310	45 038
30	14 784	7925	17 515	1284	2322	45 113
35	15 027	7699	17 687	1205	2338	45 196
40	15 325	7435	17 885	1121	2359	45 320
45	15 691	7136	18 119	1032	2386	45 523
50	16 137	6808	18 399	940	2422	45 832

as given in the last column of Table III, is also shown in Fig 6. For low Z we recognize the nonrelativistic $(a+b/Z)$ behavior, while for higher Z values an additional term with an $\alpha^2 Z^2$ behavior starts to be important. Since the p and s excitations have such different behavior one might suspect that the mixture between these states, which enters in higher orders, should be able to somewhat change the slope. This might then bring the values closer to the calculation of Gorceix *et al.*,[35] at least for medium heavy Z. They have performed Multiconfiguration Dirac-Fock (MCDF) calculations including up to $4f^2$ excitations and found a Z dependence of the electrostatic energy which is essentially flat in the region of intermediate Z, but with a maximum appearing at $Z=24$ and a local minimum at $Z=45$. The difference compared to this work is essentially a much flatter curve above $Z=20$, indicating smaller relativistic contributions.

2. *Magnetic correlation*

In Table IV the magnetic correlation is shown, and it seen that, although small for small Z, it grows fast, and for $Z=50$ the magnetic correlation is about the same size as the total, nonrelativistic and relativistic, electrostatic correlation. This is illustrated in Fig. 6. The values obtained here agree reasonably well, within 10%, with the result for magnetic correlation obtained with MCDF,[35] for medium heavy ions. The difference can probably be explained with contributions to higher order in the Coulomb interaction, which are included in MCDF when the wave functions are varied. For the largest Z there is, however, an increasing discrepancy, which presumably has another source; the MCDF result shows, then, larger magnetic correlation.

VI. CONCLUSIONS

It has been possible to show how the method of solving inhomogeneous differential equations can be used, even in the relativistic case, to obtain accurate results. As has been discussed in earlier works,[12] the method is free from any problem with continuum dissolution, and the correlation, which is treated inside the no-(virtual-)pair approximation, is correct to order α^2 Ry. All one-particle effects are, however, treated fully relativistically and the neglected α^4 Ry terms are only affecting the correlation. Such terms are presumably quite negligible for a wide range of atomic systems. At least for neutral and moderately ionized atoms the treatment of the Coulomb interaction to high orders is assumed to be of much greater significance.

The method has been applied to a wide range of two-electron systems, giving second-order energies for both electrostatic and magnetic interaction. In the near future we hope to be able to present calculations on heavy neutral atoms. The challenge is to apply the method to those systems for calculating, e.g., parity violation and hyperfine structure, where both correlation and relativistic effects are known to be important.

Some effects in this work are also treated to all orders, i.e., nonperturbatively, in Coulomb interaction. For highly ionized systems such higher-order contributions are not very important. As mentioned, however, for neutral systems they may be quite significant. The aim is to obtain a scheme allowing couplings to all orders, as has previously been possible in the nonrelativistic case. The relativistic generalization of such a scheme is in principle straightforward from this point, the only problem being a growing complexity and need for computing time.

ACKNOWLEDGMENTS

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TABLE IV. Second-order magnetic correlation (one order in magnetic and one order in electrostatic interaction) obtained with Dirac-Fock orbitals, given in units of 10^{-6} a.u., all contributions are given with opposite sign.

$1s^2$ to Z	s^2	$p_{1/2}^2$	$p_{3/2}^2$	$d_{3/2}^2$	$d_{5/2}^2$	total, $l_{\max}=4$
2	12	12	13	4	3	50
5	95	109	117	32	27	424
10	409	483	523	138	115	1851
15	936	1107	1216	308	260	4227
20	1668	1952	2193	530	458	7472
25	2597	2983	3450	788	705	11 503
30	3715	4157	4989	1068	997	16 239
35	5016	5430	6814	1357	1334	21 608
40	6495	6757	8937	1641	1388	27 548
45	8153	8093	11 373	1908	2143	34 019
50	9991	9394	14 144	2149	2617	40 981

APPENDIX: THE SOLUTION PROCEDURE

The solution procedure for the relativistic pair equation (4.2) follows the procedure for the nonrelativistic case as given in Ref. 15; only the differences are mentioned here. A more detailed description can be found in Ref. 36.

In a conventional approach the system of equations, obtained when the derivatives in (4.2) are approximated with finite-difference formulas, would be solved directly. However, the system will consist of N^2 equations, where N is the grid size. For a typical grid of 60 points the left-hand-side matrix will then consist of approximately 10^7 elements. Since the coefficient matrix is not symmetric and not always diagonal dominant, relaxation methods sometimes fail to converge. The system must then be solved by more time-consuming and storage-requiring methods, like Gaussian elimination, even if the matrix contains mostly zeros. In Ref. 15 a method is described which reduces the system of N^2 equations to a system of only $(2N+2)$ equations; Gaussian elimination is then performed on this smaller system.

The equation is solved in an exponential grid, $r_n=\exp(x_n)$, $x_n=x_{\min}+(n-1)h$, where h is an equidistant grid step. To eliminate the first-order derivatives, which then appear, the transformation

$$\bar{\rho}(r_1,r_2)=\rho(r_1,r_2)/(r_1r_2)^{1/2}$$

is used.

1. Boundary conditions for small r values

The boundary condition close to the nucleus is the slope for small r values and Eq. (14b) in Ref. 15 is replaced with

$$[\bar{\rho}^{LL}(r_1,r_2)/\bar{\rho}^{LL}(r_1',r_2)] \propto (r_1^{\gamma-1/2}+br_1^{\gamma+1/2})/(r_1'^{\gamma-1/2}+br_1'^{\gamma+1/2}) \ , \tag{A1}$$

where $\gamma=[(\kappa^2-\alpha^2Z^2)^{1/2}]$ and

$$b=[(\varepsilon_1+2mc^2)(\gamma+\kappa-\alpha^2Z^2)-\varepsilon_1\alpha^2Z^2]/[Z(2\gamma+1)] \approx \begin{cases} -Z/|\kappa| & \text{for } \kappa<0 \\ 2(\gamma+\kappa)/[Z\alpha^2(2\gamma+1)] & \text{for } \kappa>0 \end{cases}$$

for a pointlike nucleus, used when analytical hydrogenlike wave functions are used as the first approximation. This behavior is also assumed when the first grid point for the pair function is taken outside the nucleus, even if the one-particle description is a numerical Dirac-Fock wave function obtained in the field from an extended nucleus. (While the one-particle function is always started well inside the nucleus, this is not always necessary for the correlation part of the wave function.)

For extended nuclei, (14b) in Ref. 15 will be as it stands,

$$[\bar{\rho}^{LL}(r_1,r_2)/\bar{\rho}^{LL}(r_1',r_2)] \propto (r_1/r_1')^{l_1+1/2} \ . \tag{A2}$$

2. Boundary conditions for large r values

At infinity the function should fall to zero exponentially. The boundary condition applied is that the first point outside the grid used is required to decrease as

$$\bar{\rho} \propto \exp\left\{-\left[|\varepsilon_a+\varepsilon_b|\left[1+\frac{\alpha^2}{4}(\varepsilon_a+\varepsilon_b)\right]\right]^{1/2} \times (r_1+r_2)\right\}/(r_1r_2)^{1/2} \ . \tag{A3}$$

The second point outside the grid used is set to zero. The exponential decay is used to smooth the sharp cutoff obtained when immediately setting everything outside the grid area to zero, as was done nonrelativistically [(14a) in Ref. 15]. Such a cutoff is not justified in relativistic calculations. However, the wave function is so small at these distances that the modification does not seem to be very important.

3. Recursion formula for the pair function

In Eq. (16) in Ref. 15 $\bar{\rho}_{i+1,j}$ is expressed in a recursion formula in terms of $\bar{\rho}_{i,j}$, $\bar{\rho}_{i-1,j}$, and $\bar{\rho}_{i,j\pm1}$. Such a form cannot be constructed in the relativistic case if the cross-derivative term, the third line on the left-hand side in (4.2), is approximated with symmetric finite difference formulas. In order to circumvent this problem the cross derivative is in this work approximated with a *nonsymmetrical* formula in one direction and a symmetrical formula in the other. Corrections compared to symmetrical five-point formulas are added on the right-hand side, as is also done for the second-order derivatives. This results in a final numerical error proportional to h^4. The equation is solved in two different grid sizes, typically 60×60 and 80×80 points, and Richardson extrapolation is used to remove the h^4 error.) Equation (16) in Ref. 15 is then replaced with

$$\begin{aligned}\bar{\rho}_{i+1,j}=[\,&(2F_{ij}^{(1)}+2F_{ij}^{(2)}-C_{ij}-4A_{ij})\bar{\rho}_{i,j}-(A_{ij}+F_{ij}^{(2)})(\bar{\rho}_{i,j+1}+\bar{\rho}_{i,j-1})\\&+2A_{ij}(\bar{\rho}_{i-1,j+1}+\bar{\rho}_{i-1,j-1})-A_{ij}(\bar{\rho}_{i-2,j+1}+\bar{\rho}_{i-2,j-1})\\&+2h^2G_{ij}]/(F_{ij}^{(1)}-2A_{ij})-\bar{\rho}_{i-1,j}\ ,\end{aligned}\tag{A4}$$

where

$$F_{ij}^{(1)}=\frac{1}{r_1^2}\left[1+\frac{\alpha^2}{2}B_1B_2\frac{1}{r_2^2}(\kappa_2+1/2)^2+\frac{\alpha^4}{8}B_1B_2(B_{ab}+2B_2)\frac{\partial V_2}{\partial r_2}\frac{1}{r_2}(\kappa_2+1)\right]\ .\tag{A5}$$

$F^{(2)}$ is obtained by interchanging indices 1 and 2. The leading term in $F^{(1)}$ is obtained also in the nonrelativistic case and comes from the function in front of the ordinary second-order derivative in (4.2). The second and third terms arise from the cross-derivative term in (4.2). B_{ab} is defined in (3.4) and B_i in (4.5). The factor

$$A_{ij}=\frac{\alpha^2}{2h^2}\frac{1}{r_1^2r_2^2}B_1B_2\tag{A6}$$

comes from the cross-derivative term. G_{ij} denotes the right-hand side of (4.2). C_{ij} contains all terms, including ordinary potentials and centrifugal terms as well as spin-orbit terms, which act directly on the wave function,

$$\begin{aligned}C_{ij}=2h^2&\left[\varepsilon_a+\varepsilon_b-V_1-V_2+\frac{\alpha^2}{2}(\varepsilon_a+\varepsilon_b-V_1-V_2)^2+\tfrac{1}{2}\left[\frac{(\kappa_1+1/2)^2}{r_1^2}+\frac{(\kappa_2+1/2)^2}{r_2^2}\right]\right]\\&+h^2\Bigg[\frac{\alpha^2}{2}B_{ab}\left[\frac{\partial V_1}{\partial r_1}\frac{1}{r_1}(\kappa_1+1)+\frac{\partial V_2}{\partial r_2}\frac{1}{r_2}(\kappa_2+1)\right]+\frac{\alpha^2}{2}B_1B_2\left[\frac{1}{r_1^2r_2^2}(\kappa_1+1/2)^2(\kappa_2+1/2)^2\right]\\&\quad+\frac{\alpha^4}{8}B_1B_2(B_{ab}+2B_1)\frac{\partial V_1}{\partial r_1}\frac{1}{r_1}(\kappa_1+1)\frac{(\kappa_2+1/2)^2}{r_2^2}+\frac{\alpha^4}{8}B_1B_2(B_{ab}+2B_2)\frac{\partial V_2}{\partial r_2}\frac{1}{r_2}(\kappa_2+1)\frac{(\kappa_1+1/2)^2}{r_1^2}\Bigg]\ .\end{aligned}\tag{A7}$$

The first line contains terms present also in the nonrelativistic case. The second line contains the spin-orbit interaction and the three last lines come from the cross-derivative term.

The Darwin-like terms in (4.2), being first-order derivatives of the wave function, are moved to the right-hand side G_{ij}. The equation is first solved without these terms and then solved again with the operator working on the previously obtained solution. This is done until convergence is obtained. Darwin-like terms also originate from the commutators of B_{ab},B_1, and B_2 in (4.4); these are treated together with the ordinary Darwin-like terms.

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$$\alpha^2[-\langle \mathbf{p}_1^4+\mathbf{p}_2^4\rangle/8+\pi Z\langle\delta(\mathbf{r}_1)+\delta(\mathbf{r}_2)\rangle/2-\pi\langle\delta(\mathbf{r}_{12})\rangle] .$$

[28] From the Breit part of the electron-electron interaction the following terms are added (Ref. 22, pp. 189–190):

$$\langle H_2\rangle+2\pi\alpha^2\langle\delta(\mathbf{r}_{12})\rangle ,$$

where

$$H_2=-\alpha^2/(2r_{12})\{\mathbf{p}_1\cdot\mathbf{p}_2+[\mathbf{r}_{12}\cdot(\mathbf{r}_{12}\cdot\mathbf{p}_1)\mathbf{p}_2]/r_{12}^3\} ,$$

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