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Relativistic all-order pair functions from a discretized single-particle Dirac Hamiltonian

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Relativistic all-order pair functions are obtained by summation over a complete set of eigenvectors to a discretized single-particle Dirac Hamiltonian. The discretization of the Dirac equation, by substituting finite-difference formulas for derivatives, is discussed in detail. It is shown how to obtain a symmetric eigenvalue problem, and a way to avoid spurious states in the spectrum is presented. The number of operations required to solve for a radial pair function is proportional to N^3, where N is the number of radial lattice points used. The method is applied to the ground state of helium using the Dirac-Coulomb Hamiltonian and the no-virtual-pair approximation. An accuracy of a few parts in 10^8 is achieved for the total energy. This accuracy allows a determination of the leading term in the partial-wave expansion of the relativistic corrections to approximately $0.075\alpha^2(l+\frac{1}{2})^{-2}$, which implies a slow convergence compared to the partial-wave expansion of the nonrelativistic energy.

I. INTRODUCTION

The demand for very accurate relativistic atomic calculations has grown rapidly in recent years.[1] For very accurate calculations on light systems or for heavier systems the correlation between the electrons, the pair correlation, needs to be calculated relativistically. In phase with these demands we present in this paper a method to calculate relativistic pair correlation to all orders.

Previously a method to calculate pair correlation nonrelativistically to all orders has been developed in our research group.[2-4] This procedure is based on the solution of inhomogeneous radial one-particle and two-particle (pair) equations.[5,2] The most recent progress is based on a coupled-cluster procedure, including all single- and double-excitation clusters, which has been applied on four-electron systems.[6]

The solution of the nonrelativistic pair equation has been extended to the relativistic case by Lindroth *et al.*,[7] using a method based on the reduction of the full relativistic pair equation to a Schrödinger-like equation for the large-large component. Approximate energy projection operators, correct to order α^2, were used.

Here we explore a more direct method for obtaining relativistic pair functions. In this method, which is an extension of the nonrelativistic case,[8] the pair functions are obtained from a numerical orbital basis set by explicit summation over the positive-energy states. No explicit energy projection operators are needed. The effect of such operators is trivially obtained by restrictions in the summations.

The numerical basis set is obtained by discretizing the radial single-particle Dirac equation, using finite-difference formulas, leading to a matrix eigenvalue problem. We show how this can be done to obtain a symmetric eigenvalue problem and how spurious states[9,10] can be avoided. The discrete spectrum forms a complete basis on the discretized space and includes both positive- and negative-energy solutions. The method to obtain a finite single-particle spectrum has similarities with the *B*-spline method used by Johnson, Blundell, and Sapirstein.[11]

To test our new method, calculations have been performed on the ground state of helium. Comparison is made with our corresponding nonrelativistic results,[8] and with very accurate nonrelativistic calculations, combined with an evaluation of the leading corrections due to relativistic effects given by the Pauli approximation.[12,13]

In Sec. II the discretization of the single-particle Dirac equation is discussed. The method of using pair functions is described in Sec. III and numerical results for the helium ground state are given in Sec. IV. Finally some conclusions are presented in Sec. V.

II. A DISCRETE DIRAC HAMILTONIAN

Numerical basis sets have been used in atomic calculations for a long time.[14] Usually these basis sets are derived considering the total space, which is quite unnecessary for the description of a bound-state wave function. This leads to an infinite number of bound-state orbitals and a continuous set of free orbitals which has to be approximated by choosing a finite number of these orbitals.

In the nonrelativistic case we have shown how a finite number of orbitals can be generated which is complete on a discretized space.[8] Our way to view the problem is to consider the atom placed in a spherical box, large enough not to disturb the bound-state wave function considered. Inside the sphere we discretize the radial coordinate by choosing a lattice of N radial points. It is then possible to formulate a symmetric eigenvalue problem generating a basis of N radial orbitals, which are orthogonal and form a complete basis on the discretized space. For details see the nonrelativistic paper, Ref. 8.

In this work the ideas above are extended to the relativistic case. Mostly this extension is straightforward, but a problem with spurious states,[9,10] not encountered in the nonrelativistic case, is faced. The problem with spurious states is discussed in Sec. II A where we also show how we have avoided such states. In Sec. II B the discretization of the radial Dirac equation is discussed, and it is shown how this can be done without destroying the Hermiticity.

A. Spurious states

There are several different origins of spurious states occurring in the Dirac spectrum.[9] In our approach they seem to have an origin similar to that in lattice gauge field theory,[15] where it is well known that, in the spectrum of a discretized Dirac equation, spurious states might appear, an artifact known as fermion doubling.[16] An equation for a massless fermion field on a $(D+1)$-dimensional lattice (D spatial dimensions and one time dimension) will describe not one but 2^D fermions if no precautions are taken.[17]

We have investigated the problem with fermion doubling in a more pragmatic way and have found a problem with spurious states arising from the implicit second-order derivative in a system of two coupled first-order differential equations. To discuss this in more detail we examine the case of a one-dimensional Dirac equation for a free electron on a linear lattice:

$$\begin{bmatrix} mc^2 & -c\dfrac{d}{dx} \\ c\dfrac{d}{dx} & -mc^2 \end{bmatrix} \begin{bmatrix} f(x) \\ g(x) \end{bmatrix} = E \begin{bmatrix} f(x) \\ g(x) \end{bmatrix} . \tag{1}$$

Approximating the derivatives according to

$$f_i' = \frac{1}{2h}(f_{i+1} - f_{i-1}) ,$$

where h is the space between adjacent lattice sites, and eliminating g in Eq. (1), gives an equation for f_i,

$$-\frac{1}{2m}\left[\frac{f_{i+2} - 2f_i + f_{i-2}}{4h^2}\right] = \varepsilon\left[1 + \frac{\varepsilon}{2mc^2}\right] f_i ,$$

$$E = \varepsilon + mc^2 .$$

The left-hand side is the kinetic energy

$$\left.\frac{p_x^2}{2m} f(x)\right|_{x=i} = -\frac{1}{2m}\left[\frac{f_{i+2} - 2f_i + f_{i-2}}{4h^2}\right] . \tag{2}$$

The problem with this second-order derivative is that is does not connect the even and the odd lattice sites. The solution with the highest energy that can be represented on the lattice behaves roughly as

$$\cdots \approx f_{i-2} \approx -f_{i-1} \approx f_i \approx -f_{i+1} \approx f_{i+2} \approx \cdots .$$

Thus using Eq. (2) to calculate the kinetic energy will be the same as taking the derivative of a function with no nodes. This means that a high-energy eigenvector can appear as a spurious state in the low-energy part of the eigenvalue spectrum.

We have examined two approaches to overcome this problem, namely, to use either forward and backward difference formulas

$$f_i' = \frac{1}{h}(f_{i+1} - f_i), \quad g_i' = \frac{1}{h}(g_i - g_{i-1})$$

or to let the large and small components be defined on alternating sites of the lattice

$$\cdots \quad f_{i-3} \quad g_{i-2} \quad f_{i-1} \quad g_i \quad f_{i+1} \quad g_{i+2} \quad \cdots , \tag{3}$$

with h running from site g_{i-2} to g_i in the above sequence and

$$f_i' = \frac{1}{h}(f_{i+1} - f_{i-1}) ,$$

$$g_j' = \frac{1}{h}(g_{j+1} - g_{j-1}) \begin{cases} i = 2n - 1 \\ j = 2n, \quad n = 1, 2, \ldots, N . \end{cases}$$

In the work by Stacey[17] it is shown that these methods are equivalent in the sense that they reduce to the same second-order equation. Unfortunately, as demonstrated below, this is not the case if higher-order difference formulas are used.

Adopting the latter alternative with f and g defined on alternating lattice sites, and using the four-point difference formula

$$f'(x) = \frac{1}{24h}\left[f(x - \tfrac{3}{2}h) - 27f(x - \tfrac{1}{2}h) + 27f(x + \tfrac{1}{2}h) - f(x + \tfrac{3}{2}h)\right] + O(h^4) \tag{4}$$

leads to the following expression for the kinetic energy, corresponding to Eq. (2):

$$\left.\frac{p_x^2}{2m} f(x)\right|_{x=i} \approx -\frac{1}{2m}\frac{1}{12h^2}(0.02f_{i-6} - 1.12f_{i-4} + 16.3f_{i-2} - 30.4f_i + 16.3f_{i+2} - 1.12f_{i+4} + 0.02f_{i+6}) .$$

This is very close to the ordinary five-point formula[18] for the second-order derivative having the integer coefficients -1, 16, -30, 16, and -1. On the contrary, the large and small component can be defined at the same lattice sites and derivatives replaced by four-point backward and forward difference formulas for the large and small component, respectively. This gives the coefficients -0.66, 3.00, 6.00, -16.6, 6.00 3.00, and -0.66 in the resulting formula for the second-order derivative. Due to the same sign on two adjacent coefficients this formula will not count the correct number of nodes on a high-energy eigenvector and a spurious state can occur in the spectrum. This we have tested and confirmed empirically in the case of the discretized radial Dirac equation. The conclusion is that spurious states introduced by the discrete representation of the derivatives can be avoided if the discretization is done according to Eqs. (3) and (4).

B. Discretization

In the phase convention used, the single-particle Dirac wave function takes the form

$$\Psi_{n\kappa m}(\mathbf{r},\sigma)=\frac{1}{r}\begin{bmatrix} f_{n\kappa}(r)X_{\kappa m}(\theta,\phi,\sigma) \\ ig_{n\kappa}(r)X_{-\kappa m}(\theta,\phi,\sigma)\end{bmatrix},$$

where $X_{\kappa m}$ is an ls-coupled spherical harmonic spinor. The radial part of the Dirac equation can be written, using atomic units $e=m_e=\hbar=4\pi\varepsilon_0=1$, $\alpha=1/c$,

$$\begin{bmatrix} V(r) & -c\left[\dfrac{d}{dr}-\dfrac{\kappa}{r}\right] \\ c\left[\dfrac{d}{dr}+\dfrac{\kappa}{r}\right] & V(r)-2mc^2 \end{bmatrix}\begin{bmatrix} f(r) \\ g(r)\end{bmatrix}=\varepsilon\begin{bmatrix} f(r) \\ g(r)\end{bmatrix}, \tag{5}$$

which could be discretized using a linear lattice. However, in order to get a good description of the wave function close to the nucleus, a logarithmic lattice is used ($r=e^x$ with a linear lattice in x instead of r). To preserve the hermiticity of the Hamiltonian when discretized we make the transformation

$$y(r)\to\frac{1}{\sqrt{r}}y(x)$$

for both f and g. With this transformation Eq. (5) becomes

$$\begin{bmatrix} V(r) & -c\left[\dfrac{1}{\sqrt{r}}\dfrac{d}{dx}\dfrac{1}{\sqrt{r}}-\dfrac{\kappa}{\sqrt{r}}\dfrac{1}{\sqrt{r}}\right] \\ c\left[\dfrac{1}{\sqrt{r}}\dfrac{d}{dx}\dfrac{1}{\sqrt{r}}+\dfrac{\kappa}{\sqrt{r}}\dfrac{1}{\sqrt{r}}\right] & V(r)-2mc^2 \end{bmatrix}\begin{bmatrix} f(x) \\ g(x)\end{bmatrix}=\varepsilon\begin{bmatrix} f(x) \\ g(x)\end{bmatrix}.$$

Since we have defined f and g on alternating lattice sites we have to use an interpolation formula for the κ terms. The six-point formulas used for differentiation and interpolation of $(1/\sqrt{r})f(x)$ and $(1/\sqrt{r})g(x)$ are given in the Appendix, Eqs. (A1) and (A2). The discretization according to these equations gives a $2N\times 2N$ symmetric eigenvalue problem

$$\begin{bmatrix} A & D^T+K^T \\ D+K & B\end{bmatrix}\begin{bmatrix} F \\ G\end{bmatrix}=\varepsilon\begin{bmatrix} F \\ G\end{bmatrix}. \tag{6}$$

The submatrices in Eq. (6) are given in the Appendix by Eqs. (A3)–(A5). Here the discretized eigenvectors are

$$(F,G)=(f_1,f_3,\ldots,f_{2N-1},g_2,g_4,\ldots,g_{2N}), \tag{7}$$

where $f_i=f(x_i)$ and $g_i=g(x_i)$.

The boundary conditions need special attention. For the differentiation and interpolation in the first and last few points, one need to know f and g in a few points outside the N lattice points chosen for each component. Since the sphere is chosen so that the atomic wave function is negligible outside the sphere, it is natural to assume f and g to be zero beyond the last lattice point. We have not encountered any problems with this. Close to the nucleus, corresponding to the upper left corner of D, f and g can for a point nucleus be approximated by

$$f(r)\propto r^{\gamma+1/2}+\frac{2[\gamma+\kappa-(Z\alpha)^2]}{Z\alpha^2(2\gamma+1)}r^{\gamma+3/2}+\left[\frac{\gamma+\kappa-2(Z\alpha)^2}{Z(2\gamma+1)}\varepsilon r^{\gamma+3/2}\right], \tag{8a}$$

$$g(r)\propto \frac{\gamma+\kappa}{Z\alpha}r^{\gamma+1/2}-\frac{2(\gamma+\kappa)}{\alpha(2\gamma+1)}r^{\gamma+3/2}-\left[\frac{\alpha(2\gamma+2\kappa+1)}{(2\gamma+1)}\varepsilon r^{\gamma+3/2}\right], \tag{8b}$$

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

It is desirable to avoid energy-dependent corrections to the eigenvalue problem of Eq. (6), and therefore the energy-dependent terms within parenthesis, Eq. (8), have been excluded. This is a good approximation for positive bound-state energies, except for $\kappa<0$, when, in Eq. (8b), the second and third terms can be of the same order. The spectrum is intended for the description of bound atomic wave functions with energies small compared to mc^2 and the boundary conditions for these wave functions are consistent with the approximation above.

Using Eqs. (8a) and (8b) the value of g in the needed points outside the lattice can be expressed in terms of f in the first few points on the lattice according to

$$g(x_0)=\beta_1\left[\frac{g(x_0)}{f(x_1)}\right]f(x_1)+\beta_3\left[\frac{g(x_0)}{f(x_3)}\right]f(x_3)$$
$$+\beta_5\left[\frac{g(x_0)}{f(x_5)}\right]f(x_5)\ , \tag{9a}$$

$$g(x_{-2})=\gamma_1\left[\frac{g(x_{-2})}{f(x_1)}\right]f(x_1)$$
$$+\gamma_3\left[\frac{g(x_{-1})}{f(x_3)}\right]f(x_3)\ , \tag{9b}$$

$$g(x_{-4})=\left[\frac{g(x_{-4})}{f(x_1)}\right]f(x_1)\ , \tag{9c}$$

where the ratios are evaluated using Eqs. (8a) and (8b) and

$$\beta_1+\beta_3+\beta_5=\gamma_1+\gamma_3=1\ .$$

This leads to corrections to the upper left corner of the matrix A. These corrections can be made symmetric by choosing the weighting coefficients β_i and γ_i appropriately. We have chosen to treat the corrections originating from the differentiation (D) and the interpolation (K) terms separately, thus evaluating different sets of β_i and γ_i for these two terms. By the ansatz of Eqs. (9a)–(9c) the solution for the weighting coefficients is then unique when demanding symmetric corrections to the eigenvalue problem. The treatment of f outside the lattice is done analogously, with the only difference being that only two values, $f(x_{-1})$ and $f(x_{-3})$, are needed. In this work a point nucleus is assumed. Using an extended nucleus only affects Eqs. (8a) and (8b), which then have to give the correct dependence of the orbitals inside the nucleus.

By rearranging the elements of F and G according to

$$(F,G)\rightarrow(f_1,g_2,f_3,g_4,\ldots,f_{2N-1},g_{2N})\ ,$$

and the equations correspondingly, a band matrix can be achieved. Now, by diagonalizing the symmetric $2N\times 2N$ matrix in Eq. (6) one obtains an orthogonal basis set of N positive- and N negative-energy orbitals and their eigenvalues. It also follows from matrix algebra that this basis set is complete in the sense that any function can be represented exactly on the lattice. By extrapolation from lattices with different spacings the accuracy can be increased, approaching the exact description on the continuous space. This kind of extrapolation is needed if a high accuracy is demanded and can be made in a systematic way.

III. PAIR FUNCTIONS

Nonrelativistically the ground state of helium can be obtained as a solution of the Schrödinger equation

$$H\Psi(1,2)=E\Psi(1,2)\ , \tag{10}$$

where the Hamiltonian can be divided into a single-particle Hamiltonian h_0, for each electron, describing the motion in the nuclear potential and the Coulomb repulsion between the electrons $V_{12}=1/r_{12}$

$$H=h_0(1)+h_0(2)+V_{12}\ . \tag{11}$$

A first approximation of Ψ can be obtained by neglecting V_{12}, leading to an independent-particle solution Ψ_0,

$$\Psi_0(1,2)=\{\Phi_a(1)\Phi_b(2)\}=|\{ab\}\rangle=|\{1s^2\}\rangle\ , \tag{12}$$

where Φ_a and Φ_b are eigenfunctions of h_0,

$$h_0\Phi_c=\varepsilon_{1s}\Phi_c,\quad c=a,b\ , \tag{13}$$

corresponding to $m_j=\pm\frac{1}{2}$, respectively, and the curly brackets denote antisymmetrization. Both space and spin coordinates are implied by the numbers within parentheses. The part of Ψ that goes beyond the independent-particle model can be expressed in terms of a pair function $\eta_{ab}(1,2)\equiv\eta_{ba}(2,1)$ according to

$$\Psi=\{\Phi_a(1)\Phi_b(2)+\eta_{ab}(1,2)\}\ , \tag{14}$$

and we define here the correlation energy E_c by

$$E=2\varepsilon_{1s}+E_1+E_c\ , \tag{15}$$

where $E_1=R^0(1s^2,1s^2)$. Substituting Eqs. (11)–(15) into Eq. (10) and rearranging the terms leads to an equation for $\{\eta_{ab}\}$

$$[2\varepsilon_{1s}-h_0(1)-h_0(2)]|\{\eta_{ab}\}\rangle$$
$$=\frac{1}{r_{12}}|\{1s^2+\eta_{ab}\}\rangle-(E_1+E_c)|\{1s^2+\eta_{ab}\}\rangle\ . \tag{16}$$

Using intermediate normalization, $\langle\Psi_0|\Psi\rangle=\langle\Psi_0|\Psi_0\rangle=1$, the following expression for E_c is achieved by projecting Eq. (16) on $\langle\{1s^2\}|$:

$$E_c=\left\langle\{1s^2\}\left|\frac{1}{r_{12}}\right|\{1s^2+\eta_{ab}\}\right\rangle-E_1$$
$$=\left\langle\{1s^2\}\left|\frac{1}{r_{12}}\right|\{\eta_{ab}\}\right\rangle\ . \tag{17}$$

Instead of working with the antisymmetrized function $\{\eta_{ab}\}$ one can work with the nonantisymmetrized pair function η_{ab}. Taking η_{ab} as the solution to the following equation, the pair equation,

$$[2\varepsilon_{1s}-h_0(1)-h_0(2)]|\eta_{ab}\rangle$$
$$=\frac{1}{r_{12}}|ab+\eta_{ab}\rangle-|ab+\eta_{ab}\rangle\left\langle ab\left|\frac{1}{r_{12}}\right|ab+\eta_{ab}\right\rangle$$
$$-|ba+\eta_{ba}\rangle\left\langle ba\left|\frac{1}{r_{12}}\right|ab+\eta_{ab}\right\rangle\ , \tag{18}$$

one easily verifies that $\{\eta_{ab}\}$ satisfies Eq. (16).

The solution to the pair equation, Eq. (18), can be expanded in a complete set of orbitals generated by h_0, including both the bound states and the continuum part of the spectrum,

$$h_0|r\rangle=\varepsilon_r|r\rangle\ , \tag{19}$$

$$\eta_{ab}=\sum_{r,s}^{\text{virt}}\frac{|rs\rangle\langle rs|\mathcal{R}\rangle}{2\varepsilon_{1s}-\varepsilon_r-\varepsilon_s}\ , \tag{20}$$

where $\mathcal{R}$ is the right-hand side (rhs) of Eq. (18) and the sum is restricted to virtual pair states, and thus $r,s\neq a,b\,;b,a$. We let here the summation also denote the integration over the continuum part of the spectrum. Equation (20) is an implicit expression for η_{ab} (since $\mathcal{R}$ depends on η_{ab}) and η_{ab} can be obtained iteratively. A first approximation is achieved by neglecting the dependence of η_{ab} in the rhs giving

$$\eta_{ab}\approx\sum_{r,s}^{\text{virt}}\frac{|rs\rangle\left\langle rs\left|\frac{1}{r_{12}}\right|ab\right\rangle}{2\varepsilon_{1s}-\varepsilon_r-\varepsilon_s}\ . \tag{21}$$

Relativistically we want to use Dirac Hamiltonians

$$h_0(i)=c(\boldsymbol{\alpha}\cdot\mathbf{p})_i+mc^2(\beta-1)_i-\frac{Z}{r_i}$$

for the single-particle Hamiltonians in Eqs. (11) and (19) when generating the pair function η_{ab} iteratively using Eq. (20). With the use of this h_0, however, having both a positive- and a negative-energy spectrum, the derivation above leading to Eq. (16) is doubtful. As pointed out by Brown and Ravenhall[19] the relativistic time-dependent counterpart of Eq. (10) has no stationary solutions due to the possibility of real transitions to states where one electron has a negative energy and the other electron is far up in the positive-energy continuum. For the time-independent equation, Eq. (10) or Eq. (18), this means that there are no normalizable solutions due to an infinite degeneracy of the bound two-particle states, with states having one negative-energy electron and one positive-energy electron. The direct addition of the Coulomb interaction to the independent-particle Dirac equation is obviously not based on correct physical assumptions. The missing physics is that the idea in Dirac's hole theory of a filled engative-energy sea is not incorporated in our equations and excitations to negative-energy states [e.g., r or s being negative-energy states in Eq. (21)] will incorrectly be allowed. The cure devised already by Brown and Ravenhall[19] and later advocated by Sucher[20] is to deduce an equation in the framework of QED. In QED the second quantization of the interaction field and the matter field incorporates to the full the ideas of Dirac's hole theory.

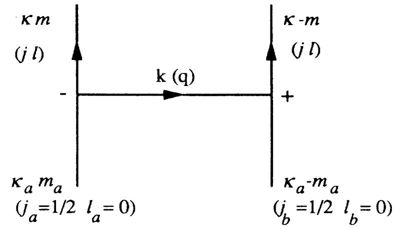

FIG. 1. Angular momentum graph (Ref. 4) corresponding to $G^k(\kappa,m,a,b)$ in the partial-wave expansion, Eq. (22), of a $1s^2$ state, and thus $\kappa_a=\kappa_b=-1$ and $m_a=-m_b=\pm\frac{1}{2}$. Each vertex represents a 3-j symbol involving j and m of the free lines and k and q of the internal line. The k and q come from the partial-wave expansion of the Coulomb interaction (Ref. 4). The summation over q is implicitly assumed in the graph.

In Dirac's hole theory excitations to the occupied negative-energy states are forbidden. On the other hand, excitations from the negative-energy states, creating electron-positron pairs, are allowed. In this work the "no-virtual-pair" approximation, omitting these excitations from the negative-energy states, is used. Such excitations contribute to order α^3 Ry.[21] In the framework of this approximation, Eqs. (20) and (21) are correct, provided the summations are restricted to positive-energy states. Formally this is equivalent to having positive-energy projection operators surrounding V_{12} in Eq. (11).[20]

Recently Lindroth *et al.*[7] have solved the pair equation, Eq. (18), by reduction to a Schrödinger-like equation for the large-large component and then solved directly as an inhomogeneous differential equation. Energy projection operators were needed and these are only known approximately in closed form, although correct to order α^2 Ry. With the method presented in this work, however, there are no problems with projection operators, since the spectrum is known explicitly. Thus this method can be extended beyond the no-virtual-pair approximation.

The evaluation of the pair function using the finite spectrum has been carefully described for the nonrelativistic case.[8] In the relativistic case the pair function η_{ab}, describing corrections to the $1s^2$ state, can be expanded in partial waves according to

$$\eta_{ab}(1,2)=\sum_{k,\kappa}\sum_{m}\begin{bmatrix}X_{\kappa m}(1) & 0\\ 0 & iX_{-\kappa m}(1)\end{bmatrix}\begin{bmatrix}\rho_{LL}^{\kappa k}(r_1,r_2) & \rho_{LS}^{\kappa k}(r_1,r_2)\\ \rho_{SL}^{\kappa k}(r_1,r_2) & \rho_{SS}^{\kappa k}(r_1,r_2)\end{bmatrix}\begin{bmatrix}X_{\kappa,-m}(2) & 0\\ 0 & iX_{-\kappa,-m}(2)\end{bmatrix}G^k(\kappa,m,a,b)\ , \tag{22}$$

where $X_{\kappa m}$ is an ls-coupled spherical harmonic spinor and G^k is represented by the angular momentum diagram[4] in Fig. 1. Here κ is

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

and κ is the same in both coordinates, since the total angular momentum of the $1s^2$ state considered is zero and the Coulomb interaction preserves parity. For each partial wave, determined by κ and k, one radial pair function is needed. From the angular momentum diagram in Fig. 1 the possible values for k are deduced

$$k=j\pm\tfrac{1}{2} \tag{23}$$

using triangular conditions.

The lowest-order approximation of η_{ab} was given in Eq. (21). Using the standard partial-wave expansion of the Coulomb interaction[4]

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

and the expansion of η_{ab} in Eq. (22), leads to the following expression for the lowest-order radial pair function:

$$\rho^{\kappa k}(r_1,r_2)=\begin{bmatrix}\rho_{LL} & \rho_{LS}\\ \rho_{SL} & \rho_{SS}\end{bmatrix}^{\kappa k}$$

$$=\sum_{n_1,n_2}^{\text{virt}} \begin{bmatrix}F(r_1)\\ G(r_1)\end{bmatrix}^{n_1\kappa} [F(r_2),G(r_2)]^{n_2\kappa} \frac{\langle n_1\kappa n_2\kappa | r_<^k/r_>^{k+1} | 1-1,1-1\rangle}{2\varepsilon_{1s}-\varepsilon_{n_1\kappa}-\varepsilon_{n_2\kappa}}(-1)^k\langle\kappa\|\mathrm{C}^k\|-1\rangle^2 \,. \tag{24}$$

Here F and G are the large (L) and small (S) radial components of the spectrum orbitals. The radial pair functions $\rho^{\kappa k}$ are symmetric and consist of four components corresponding to the four possible products of the large and small components of the orbitals. For a nonzero value of the reduced matrix element of the C^k tensor in Eq. (24), $l+k+0$ (notations of Fig. 1) has to be even. This restricts k of the lowest-order radial pair functions to a single value for each κ. Using the full rhs of Eq. (18), however, both possibilities of k given in Eq. (23) contribute.

Despite the fact that, relativistically, the spectrum orbitals have two radial components, and the radial pair functions accordingly have four radial components, most of the procedure is equivalent to the nonrelativistic case. The two radial components of the spectrum orbitals, being defined on N lattice points each, can be combined and regarded as vectors with $2N$ elements, as in Eq. (7). These vectors are eigenvectors of the discretized Hamiltonian in Eq. (6) and are orthogonal, using a simple scalar product. In the same way the four radial components of a radial pair function can be combined into a single matrix $\rho_{ij}^{\kappa k}$ with $2N\times 2N$ elements [see Eq. (24)]. The same is true for the radial parts in a partial-wave expansion of the rhs in Eq. (18), used in Eq. (20) when evaluating the pair function. As in the nonrelativistic case[8] a radial pair function can then be obtained as a simple sum of overlaps of the spectrum orbitals with the corresponding radial rhs originating from Eq. (18).

In the no-virtual-pair approximation, summing over N positive-energy eigenvectors for each radial coordinate, approximately $12N^3$ multiplications are needed to evaluate a radial pair function. This should be compared with the nonrelativistic case for which $4N^3$ multiplications are needed, only a factor of 3 different from the relativistic case. The CPU time needed to solve for one relativistic pair function is about 30 s on a SUN 4/110 work station. The number of pair functions needed is, however, a factor of 4 larger than in the nonrelativistic case (two κ values, each with two k values, for excitations to a specific l value). The total amount of computing time is thus roughly a factor of 12 larger than that for the nonrelativistic case. In practice, the factor is somewhat larger than 12 due to the increased part of the total time needed for evaluating the right-hand sides.

IV. RESULTS

In this section relativistic second-order and all-order helium results are presented for the Coulomb correlation energy in the no-virtual-pair approximation. Only the Coulomb interaction has thus been treated, and other effects such as Breit interaction, the Lamb shift, and finite nuclear mass effects have so far been omitted. The results given can therefore not be compared directly with experiment, but a comparison can be made with the very accurate results of Pekeris[12] or Drake.[13] Their results come from very accurate nonrelativistic calculations combined with an evaluation of all the leading corrections due to relativistic effects, which are of order α^2 and given by the Pauli approximation. The relevant terms to compare with are, following Bethe and Salpeter,

$$H_1=-\frac{\alpha^2}{8}(\mathbf{p}_1^4+\mathbf{p}_2^4)$$

and

$$H_4=\pi\alpha^2[Z\delta(\mathbf{r}_1)-\delta(\mathbf{r}_{12})]\,,$$

which according to Drake amount to $-0.000\,132\,11$ a.u. The main part of this comes from the relativistic α^2 contribution to the zeroth-order and the first-order energies

$$E_0=2\varepsilon_{1s}=\frac{2}{\alpha^2}\{[1-(Z\alpha^2)]^{1/2}-1\}$$

$$=-Z^2-\tfrac{1}{4}Z^4\alpha^2-\tfrac{1}{8}Z^6\alpha^4-\cdots\,, \tag{25a}$$

$$E_1=R^k(1s^2,1s^2)=Z\left[1-\frac{\Gamma(4\gamma+1)}{2^{4\gamma}\Gamma(2\gamma+1)^2}\right]$$

$$=\tfrac{5}{8}Z+\tfrac{3}{4}[1-\ln(2)]\alpha^2Z^3+\cdots\,, \tag{25b}$$

using hydrogenlike orbitals of He^+, where $\gamma=[1-(Z\alpha)^2]^{1/2}$. By subtracting these contributions from the total α^2 value of Drake, we obtain the α^2 contribution to the correlation energy which amounts to -1714×10^{-8} a.u. (see Table I).

Our calculation is based on relativistic hydrogenlike orbitals, and therefore higher-order effects beyond α^2 are included. For $E_0=-4.000\,213\,03$ a.u. and $E_1=1.250\,098\,06$ a.u. the α^4 effects are only about 2×10^{-8} a.u. and cancel almost exactly (see Table I).

TABLE I. Ground-state energy of He resolved in terms of different order of α^2. Only the Coulomb correlation energy is included as described in the text. Energies in atomic units.

	Nonrelativistic	10^8(Terms of order α^2)	10^8(Terms of order α^4)	Relativistic
$2\varepsilon_{1s}$[a]	-4	-21301	-2	$-4.000\,213\,03$
$R^k(1s^2,1s^2)$[a]	$+1.25$	$+9804$	$+2$	$+1.250\,098\,06$
Correlation	$-0.153\,724\,38$[b]	-1714[b]	<1[c]	$-0.153\,741\,52$
Total	$-2.903\,724\,38$[d]	$-132\,11$[d]	<1[b]	$-2.903\,356\,49$

[a] α^2 expansion of the analytical expressions given in Eqs. (25a) and (25b).

[b] Deduced from the other numbers in this column.

[c] An estimate based on the relative importance of α^4 contributions to $2\varepsilon_{1s}$ and $R^k(1s^2,1s^2)$.

[d] Deduced from Drake, Ref. 13.

The corresponding contribution to the correlation energy, being an order of magnitude smaller, should be less than 1×10^{-8} a.u. Therefore we expect to get agreement between the α^2 result for the correlation energy deduced from Drake and our calculation of the correlation energy.

The correlation energy is in our calculation obtained by solving the pair equation by summation in Eq. (20) over the discrete spectrum and then using Eq. (17). The range of the lattices used in the calculations presented is

$$r_{\min}=\frac{e^{-8.0}}{Z},\quad r_{\max}=\frac{e^{3.0}}{Z},\quad Z=2$$

which was found to give sufficiently small boundary effects. To achieve high numerical accuracy several lattice spacings were used and the results extrapolated to zero spacing. The correlation energy was assumed to have the same dependence on the lattice spacing as the nonrelativistic case[8]

$$E(h)\approx E(0)+a_1h^4+a_2h^5+a_3h^6+O(h^7)\ .$$

We have used four different lattices with 85, 91, 101, and 121 points, respectively. Using a single lattice with, say, 91 points, the error is about one part in 10^6 for the $l=10$ limit. Using two lattices, the h^4-dependent error can be removed, which should be sufficient for heavier systems with many electrons. The use of four lattices is only justified for two-electron systems for which the pair equation represents an exact result.

TABLE II. Partial-wave contributions to the relativistic second-order Coulomb correlation energy of He. The correlation energy is evaluated relative to $E_0+E_1=-2.750\,114\,97$ a.u. using hydrogenlike orbitals. Energies in atomic units.

l	κ	This work		Johnson and Saperstein[a]
0	-1	$-0.125\,356\,11$	$-0.125\,356\,11$	$-0.125\,356\,11$
1	1	$-0.008\,828\,32$		
	-2	$-0.017\,664\,09$	$-0.026\,492\,41$	$-0.026\,492\,41$
2	2	$-0.001\,561\,08$		
	-3	$-0.002\,343\,58$	$-0.003\,904\,65$	$-0.003\,904\,65$
3	3	$-0.000\,461\,23$		
	-4	$-0.000\,615\,71$	$-0.001\,076\,94$	$-0.001\,076\,94$
4	4	$-0.000\,180\,12$		
	-5	$-0.000\,225\,50$	$-0.000\,405\,62$	$-0.000\,405\,62$
5	5	$-0.000\,083\,86$		
	-6	$-0.000\,100\,82$	$-0.000\,184\,68$	$-0.000\,184\,67$
6	6	$-0.000\,044\,05$		
	-7	$-0.000\,051\,51$	$-0.000\,095\,56$	$-0.000\,095\,56$
7	7	$-0.000\,025\,27$		
	-8	$-0.000\,028\,96$	$-0.000\,054\,23$	$-0.000\,054\,22$
8	8	$-0.000\,015\,50$		
	-9	$-0.000\,017\,49$	$-0.000\,032\,99$	$-0.000\,032\,98$
9	9	$-0.000\,010\,02$		
	-10	$-0.000\,011\,17$	$-0.000\,021\,19$	$-0.000\,021\,19$
10	10	$-0.000\,006\,76$		
	-11	$-0.000\,007\,46$	$-0.000\,014\,22$	$-0.000\,014\,24$
$\sum_{l=0}^{10}$			$-0.157\,638\,60$	$-0.157\,638\,59$

[a] From Ref. 22.

A. Second-order results

The second-order correlation energy is obtained from the first-order pair function through Eqs. (17) and (21). The first-order pair equation decouples into independent radial equations for the different partial waves. In Table II the contributions from the different partial waves to the correlation energy are given. Comparison with results by Johnson and Sapirstein[22] show excellent agreement, indicating that the accuracy of both calculations is about one part in 10^8 for the partial-wave limits. The same accuracy is expected for the more interesting all-order partial-wave limits presented in Sec. IV B.

B. All-order results

For the all-order results, when solving the pair equation to self-consistency, we have to truncate the partial-wave expansion at some point. We have chosen to include all partial waves with l less than or equal to some value which relates directly to nonrelativistic l limits. The all-order l-limit results E_l are presented in Table III. Our s-limit result is in excellent agreement with results from Lindroth *et al.*[7] and Blundell *et al.*[23] and our p and d limits with the less accurately calculated p and d limits of Blundell *et al.* Unfortunately, the more extended table of l-limit results of Blundell *et al.* are defined differently from ours, preventing a comparison with our relativistic results and the corresponding nonrelativistic ones. Including partial waves up to $l=10$ gives the total correlation energy accurate to two parts in 10^5 (see Table III). Due to the slow l convergence it would be too tedious to increase the accuracy substantially by calculating explicitly higher l limits. The tail contribution from high partial waves thus has to be extrapolated. This extrapolation is the main limitation of the accuracy for two-electron systems.

Nonrelativistically the all-order partial-wave contribution, $\Delta E_l = E_l - E_{l-1}$, has the well-known asymptotic expansion[24]

$$\Delta E_l = D_4(l+\tfrac{1}{2})^{-4} + D_5(l+\tfrac{1}{2})^{-5} + D_6(l+\tfrac{1}{2})^{-6} + O(l^{-7}) \;, \tag{26}$$

with the coefficients[25,26,8]

$$D_4 \approx -0.074\,225\,7, \quad D_5 \approx -0.030\,989\,1 \;, \quad D_6 \approx +0.013 \;. \tag{27}$$

Trying to use a similar expansion, making a fit to the ΔE_l given in Table III, leads to a tail contribution from $l > 10$ to 1890×10^{-8} a.u. This would give a total correlation energy in error compared to the result derived from Drake (Table I) by 26×10^{-8} a.u. This error is about a factor of 10 too large compared to what would be expected with the nonrelativistic accuracy.[8]

To investigate the reason for the unexpected discrepancy above we have evaluated the true relativistic effects in the partial-wave contributions by subtracting the nonrelativistic (nonrel) results from Ref. 8. These are given in Table III and show a stable trend going to higher l limits. Assuming the following asymptotic expansion of these relativistic effects

$$\Delta E_l^{\mathrm{rel}} - \Delta E_l^{\mathrm{nonrel}} = \Delta D_k^{\mathrm{rel}}(l+\tfrac{1}{2})^{-k} + \Delta D_{k+1}^{\mathrm{rel}}(l+\tfrac{1}{2})^{-(k+1)} + \cdots \;, \tag{28}$$

TABLE III. Partial-wave contributions and limits of the relativistic all-order Coulomb correlation energy of He. The correlation energy is evaluated relative to $E_0 + E_1 = -2.750\,114\,97$ a.u. using hydrogenlike orbitals. In the last two columns, the differences to nonrelativistic (nonrel) results from Ref. 8 are given. Energies in atomic units (10^8 a.u.).

l	$\Delta E_l^{\mathrm{rel}}$	E_l^{rel}	$\Delta E_l^{\mathrm{rel}} - \Delta E_l^{\mathrm{nonrel}}$	$E_l^{\mathrm{rel}} - E_l^{\mathrm{nonrel}}$
0	−129 049 58	−129 049 58	−2080.9	−2080.9
1	−214 858 0	−150 535 37	168.4	−1912.4
2	−224 993	−152 785 30	68.5	−1844.0
3	−553 90	−153 339 20	33.2	−1810.8
4	−197 32	−153 536 52	19.3	−1791.4
5	−8698	−153 632 50	12.8	−1778.6
6	−4409	−153 667 59	8.9	−1769.7
7	−2466	−153 692 25	6.5	−1763.3
8	−1485	−153 707 10	5.1	−1758.1
9	−947	−153 716 56	3.8	−1754.4
10	−631	−153 722 88	3.4	−1751.0
$\sum_{l=11}^{\infty}$	−1866[a]		36[b]	
$\sum_{l=0}^{\infty}$		−153 741 54		−1715
Drake[c]		−153 741 52		−1714

[a] Adding the relativistic corrections from Eq. (29) to the nonrelativistic tail from Ref. 8.

[b] From Eq. (29).

[c] Deduced from Drake, Ref. 13 (see Table I).

we can deduce the leading term by making a log-log plot (Fig. 2) towards $l+1/2$. The slope of the line in Fig. 2 gives the exponent $k\approx 2.12$. Assuming integer exponents we conclude that $k=2$ (examining the second-order results also yields a $k=2$ term). This gives an extremely slow l convergence compared to the nonrelativistic expansion given by Eq. (26) for which $k=4$. The fact that the points in Fig. 2 are so well fitted by a straight line indicates that the contribution from the remaining terms in Eq. (28), which includes effects from relativistic corrections $\Delta D_4^{\rm rel}$ and $D_5^{\rm rel}$ to the nonrelativistic coefficients given in Eq. (27), is negligible. The coefficient $\Delta D_2^{\rm rel}$ can be determined by a least-squares fit giving $\Delta D_2^{\rm rel}\approx 4.0\times10^{-6}\approx 0.075\alpha^2$. This gives the tail contribution from the relativistic corrections

$$\sum_{l=11}^{\infty}(\Delta E_l^{\rm rel}-\Delta E_l^{\rm nonrel})\approx\sum_{l=1}^{\infty}4.0\times10^{-6}(l+\tfrac{1}{2})^{-2} \approx 36\times10^{-8}\ \text{a.u.} \qquad (29)$$

Adding this contribution to the $l=10$ limit of the relativistic correction from Table III we get the total relativistic correction to the Coulomb correlation energy to -1715×10^{-8} a.u., in very good agreement with the result deduced from the calculation by Drake in Table I. The nonrelativistic tail contribution from $l>10$ is -1902×10^{-8} a.u.,[8] and adding the relativistic correction gives the tail to -1866×10^{-8} a.u., as given in Table III. This gives the total Coulomb correlation energy to $-153\,741\,154\times10^{-8}$ a.u. and the total energy to $-2.903\,356\,51$ a.u.

It would be very difficult to determine the $(l+1/2)^{-2}$-dependent contribution using the total partial-wave contribution $\Delta E_l^{\rm rel}$ given in Table III, since it is overpowered by the $(l+1/2)^{-4}$ contribution [Eq. (26)]. This leads to a serious problem if high accuracy is needed, e.g., for testing QED in two-electron systems. Either one has to include very high partial waves so that the $(l+1/2)^{-2}$ term is not negligible compared to the $(l+1/2)^{-4}$ term, in the relativistic analog of Eq. (26), or perform both a non relativistic and a relativistic calculation, as done in this work. Another approach to solve the problem might be to include the correct cusp behavior in the ansatz for the wave function.

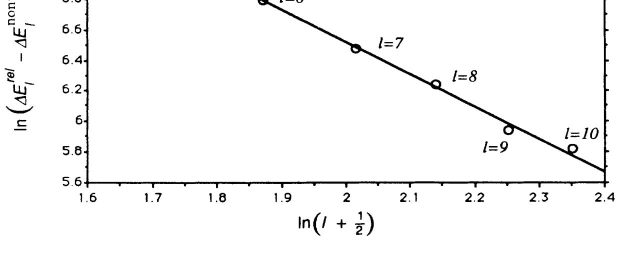

FIG. 2. Log-log plot of the relativistic corrections to the partial-wave increments of the Coulomb correlation energy of helium (from Table III).

Nonrelativistically the leading terms in the l expansion, Eq. (26), follow from the electron-electron correlation cusp condition,[27] and promising attempts to include the correct cusp behavior in the ansatz for the wave function have been made.[26] The cusp behavior for relativistic wave functions has been discussed by Kutzelnigg,[28] who finds the wave function to be more singular at $\mathbf{r}_1=\mathbf{r}_2$ in this case. This might be an explanation of the slow l convergence for the relativistic corrections.

V. CONCLUSIONS

A method to solve the relativistic pair equation has been described. The method which is an extension of the corresponding nonrelativistic one,[8] is based on summation over a finite spectrum obtained from a discretized one-particle Dirac Hamiltonian. How the discretization can be done, using finite-difference formulas, without the loss of Hermiticity has been demonstrated. By defining the large and small radial components of the spectrum orbitals on lattices shifted relative to each other, spurious states have been avoided. The Hermiticity of the eigenvalue problem generating the spectrum assures that the spectrum orbitals form a complete orthogonal basis, using a simple scalar product, on the radial lattice used. Such a spectrum is very suitable for use in perturbation theory when studying many-electron systems.

As in the nonrelativistic case it is possible to implement the method so that the number of operations needed to solve for a radial pair function is proportional to N^3, with N being the number of radial lattice points for each radial component of the spectrum orbitals. Using the no-virtual-pair approximation, the number of operations needed increases only by a factor of 3 compared to solving for a radial pair function nonrelativistically.

The new method was applied for calculating the energy of the ground state of helium, using the Dirac-Coulomb Hamiltonian in the no-virtual-pair approximation. An accuracy of a few parts in 10^8 was achieved. The most difficult problem achieving such an accuracy was to extrapolate the contribution from high partial waves. The relativisitc corrections were found to converge very slowly, showing an $(l+1/2)^{-2}$ dependence. This will be a serious problem if very high accuracy is wanted, as for two-electron systems, and well worth looking into more carefully.

A great advantage of the new method is that the positive- and negative-energy spectra are known explicitly and no explicit energy projection operators are needed. This makes the method more flexible than the previous one used by Lindroth *et al.*[7] relying on solving differential equations.

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APPENDIX

Formulas of $O(h^6)$ used for the differentiation and interpolation,

$$y'(x)=\frac{1}{1920h}[-9y(x-\tfrac{5}{2}h)+125y(x-\tfrac{3}{2}h)-2250y(x-\tfrac{1}{2}h)+2250y(x+\tfrac{1}{2}h)-125y(x+\tfrac{3}{2}h)+9y(x+\tfrac{5}{2}h)]+O(h^6), \tag{A1}$$

$$y(x)=\tfrac{1}{256}[3y(x-\tfrac{5}{2}h)-25y(x-\tfrac{3}{2}h)+150y(x-\tfrac{1}{2}h)+150y(x+\tfrac{1}{2}h)-25y(x+\tfrac{3}{2}h)+3y(x+\tfrac{5}{2}h)]+O(h^6)\ . \tag{A2}$$

The submatrices in Eq. (6) are given by

$$A_{ii}=-\frac{Z}{r_i},\quad B_{jj}=-2mc^2-\frac{Z}{r_j}\times\begin{cases} i=2n-1 \\ j=2n, \quad n=1,2,\ldots,N,\end{cases} \tag{A3}$$

$$D=\frac{c}{1920h}\begin{bmatrix} -\frac{2250}{\sqrt{r_2r_1}} & \frac{2250}{\sqrt{r_2r_3}} & -\frac{125}{\sqrt{r_2r_5}} & \frac{9}{\sqrt{r_2r_7}} & 0 & \cdots & \cdots \\ \frac{125}{\sqrt{r_4r_1}} & -\frac{2250}{\sqrt{r_4r_3}} & \frac{2250}{\sqrt{r_4r_5}} & -\frac{125}{\sqrt{r_4r_7}} & \frac{9}{\sqrt{r_4r_9}} & 0 & \cdots \\ -\frac{9}{\sqrt{r_6r_1}} & \frac{125}{\sqrt{r_6r_3}} & -\frac{2250}{\sqrt{r_6r_5}} & \frac{2250}{\sqrt{r_6r_7}} & -\frac{125}{\sqrt{r_6r_9}} & \frac{9}{\sqrt{r_6r_{11}}} & \cdots \\ 0 & -\frac{9}{\sqrt{r_8r_3}} & \frac{125}{\sqrt{r_8r_5}} & -\frac{2250}{\sqrt{r_8r_7}} & \frac{2250}{\sqrt{r_8r_9}} & -\frac{125}{\sqrt{r_8r_{11}}} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}, \tag{A4}$$

$$K=\frac{\kappa}{256}\begin{bmatrix} \frac{150}{\sqrt{r_2r_1}} & \frac{150}{\sqrt{r_2r_3}} & -\frac{25}{\sqrt{r_2r_5}} & \frac{3}{\sqrt{r_2r_7}} & 0 & \cdots & \cdots \\ -\frac{25}{\sqrt{r_4r_1}} & \frac{150}{\sqrt{r_4r_3}} & \frac{150}{\sqrt{r_4r_5}} & -\frac{25}{\sqrt{r_4r_7}} & \frac{3}{\sqrt{r_4r_9}} & 0 & \cdots \\ \frac{3}{\sqrt{r_6r_1}} & -\frac{25}{\sqrt{r_6r_3}} & \frac{150}{\sqrt{r_6r_5}} & \frac{150}{\sqrt{r_6r_7}} & -\frac{25}{\sqrt{r_6r_9}} & \frac{3}{\sqrt{r_6r_{11}}} & \cdots \\ 0 & \frac{3}{\sqrt{r_8r_3}} & -\frac{25}{\sqrt{r_8r_5}} & \frac{150}{\sqrt{r_8r_7}} & \frac{150}{\sqrt{r_8r_9}} & -\frac{25}{\sqrt{r_8r_{11}}} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}\ . \tag{A5}$$

Note that the eigenvalue problem of Eq. (6) is symmetric, although the submatrices D and K are unsymmetric.

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