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Solution of the pair equation using a finite discrete spectrum

Sten Salomonson and Per Öster
Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

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A method for the solution of the pair equation, by summation over a complete and finite basis set, is presented. The basis set is obtained by diagonalization of a discretized Hermitian one-particle Hamiltonian. The number of operations required to solve the radial pair equation is proportional to N^3 where N is the number of radial lattice points used. An application to the ground state of helium, evaluating the total energy to an accuracy of a few parts in 10^8, is presented. The method is equally well applicable to the study of pair correlation in many-electron atoms.

I. INTRODUCTION

To extract valuable information from accurate experimental results on atomic systems, accurate atomic calculations are often needed. Combining experiments and calculations, different theories can be tested and secondary information such as nuclear moments and the nuclear charge distribution can be extracted.

There are three widely used approaches to accurate atomic calculations, configuration-interaction (CI), multiconfiguration Hartree-Fock (MCHF), and many-body perturbation theory (MBPT). Despite the access of very fast computers the improvement of the accuracy and performance of these methods relies mainly on further development of their formulation and on new numerical techniques.

The diagrammatic formulation of MBPT, introduced into atomic physics by Kelly,[1] has proved to be a convenient framework for systematic calculations. Within this formulation the wave function naturally consists of building blocks describing one-particle, two-particle , . . . , n-particle excitations and all products of such excitations. An elegant formulation of this is the coupled-cluster (CC) theory.[2,3]

A procedure has been developed to solve the CC equations including all clusters for single and double excitations,[4,5] referred to as the CCSD method. This involves the numerical solution of radial one-particle and two-particle differential equations. The solution of the two-particle equation (the pair equation) is particularly demanding. A method to solve the pair equation and obtain the pair functions by direct numerical integration has been developed[6–8] and described in detail by Mårtensson.[8] The numerical solution of the pair equation originates from earlier work by McKoy and Winter.[9] The CCSD method and its implementation in a new pair program will be presented separately together with applications on four-electron systems.[5] This new pair program has been used in the present work.

In this paper we present a method to solve the radial pair equation based on summation over a finite spectrum. This spectrum is obtained by diagonalization of a discretized one-particle Schrödinger Hamiltonian. The method to obtain a finite single-particle spectrum has similarities with the B-spline method used by Johnson and Sapirstein.[10]

We test our new method on the ground state of helium to determine the numerical accuracy. Since the CCSD method is formally exact for a two-electron system we can compare our numerical results with the very accurate variational calculation by Frankowski and Pekeris,[11] recently improved by Freund *et al.*[12]

In Sec. II we derive the pair equation for the helium ground state. The problem of discretizing the one-particle Hamiltonian is discussed in Sec. III. There we show how a finite orthogonal basis set of orbitals is obtained, which is complete on the discrete space chosen, and how such a basis set conveniently can be used to evaluate the radial pair functions. The numerical results for helium are presented in Sec. IV and carefully examined in relation to the accurate variational calculations. Special attention is given to the convergence of the partial-wave expansion of the wave function. Some conclusions are presented in Sec. V.

II. PAIR FUNCTIONS

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

$$H\Psi=E\Psi \ , \tag{1}$$

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 $V_{12}=1/r_{12}$

$$H=h_0(\mathbf{r}_1)+h_0(\mathbf{r}_2)+V_{12} \ . \tag{2}$$

A first approximation of Ψ can be obtained by neglecting V_{12}, leading to an independent-particle solution Ψ_0 (since H is spin independent, we consider only the orbital space part of the wave function, which is symmetric for the ground state of helium)

$$\Psi_0(\mathbf{r}_1,\mathbf{r}_2)=\Phi_{1s}(\mathbf{r}_1)\Phi_{1s}(\mathbf{r}_2)=|1s^2\rangle \ , \tag{3}$$

where Φ_{1s} is an eigenfunction of h_0

$$h_0\Phi_{1s}(\mathbf{r})=\varepsilon_{1s}\Phi_{1s}(\mathbf{r}) \ . \tag{4}$$

We define the remaining part of Ψ as the pair function η and the part of the energy E beyond the independent-particle model (IPM) as the correlation energy E_c

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\Psi_0(\mathbf{r}_1,\mathbf{r}_2)+\eta(\mathbf{r}_1,\mathbf{r}_2) \ , \tag{5}$$

$$E=2\varepsilon_{1s}+E_1+E_c \ , \tag{6}$$

where $E_1=\langle 1s^2|1/r_{12}|1s^2\rangle$. If we substitute Eqs. (2)–(6) into Eq. (1) and rearrange the terms, we get an equation, the pair equation, for the pair function η

$$[2\varepsilon_{1s}-h_0(r_1)-h_0(r_2)]|\eta\rangle =\frac{1}{r_{12}}|1s^2+\eta\rangle-(E_1+E_c)|1s^2+\eta\rangle \ . \tag{7}$$

Integration from the left with $\langle 1s^2|$ gives the correlation energy

$$E_c=\left\langle 1s^2\left|\frac{1}{r_{12}}\right|1s^2+\eta\right\rangle-E_1=\left\langle 1s^2\left|\frac{1}{r_{12}}\right|\eta\right\rangle \ , \tag{8}$$

where we have used intermediate normalization of Ψ

$$\langle 1s^2|\Psi\rangle=1 \ .$$

The pair function η can be expanded in partial waves, using standard notations,

$$\eta(\mathbf{r}_1,\mathbf{r}_2)=\sum_{k,q}\frac{1}{r_1r_2}\rho^k(r_1,r_2)Y^k_q(\theta_1,\phi_1)Y^k_{-q}(\theta_2,\phi_2) \times(-1)^{k-q}\begin{bmatrix}k & k & 0\\ q & -q & 0\end{bmatrix}^2 \ . \tag{9}$$

For each partial wave k, one radial pair function ρ^k is required. Substituting this expansion into Eq. (7) leads to a coupled system of differential equations for the radial pair functions. To get the exact pair function η, an iterative procedure is used, since the right-hand side (rhs) of the pair equation, Eq. (7), contains η. For many years our method to obtain the radial pair functions has been a direct numerical solution of these differential equations.[8,13]

Another way to obtain the pair function is to expand η in a complete one-particle basis. Such a basis set is generated by the spectrum of h_0

$$h_0|r\rangle=\varepsilon_r|r\rangle \ .$$

By applying boundary conditions at some large distance R, the continuum part of the spectrum is represented by a discrete one. In the limit when R goes to infinity the continuous spectrum is restored. The pair function can then be expressed as, using the discrete representation of the spectrum [$\mathcal{R}$ denotes the right-hand side of Eq. (7)],

$$\eta(\mathbf{r}_1,\mathbf{r}_2)=\sum_{r,s}^{\text{virt}}\frac{|rs\rangle\langle rs|\mathcal{R}}{2\varepsilon_{1s}-\varepsilon_r-\varepsilon_s} \ , \tag{10}$$

which satisfies Eq. (7). The sum in Eq. (10) excludes the $|1s^2\rangle$ state and thus is restricted to virtual pair states, having at least one electron excited. If such a complete one-particle basis set is available, the pair function can be obtained by a simple sum of overlaps with the rhs of Eq. (7). As described above, η can be expanded in partial waves and evaluated in an iterative way. In the first approximation of the pair function, the rhs [of Eq. (7)] is

$$\mathcal{R}=\frac{1}{r_{12}}|1s^2\rangle \ , \tag{11}$$

omitting the orthogonality term which does not contribute when evaluating the pair function according to Eq. (10). The expression for the radial pair functions defined in Eq. (9) is then to lowest order, with $k=l$,

$$\rho^k(r_1,r_2)=\sum_{n,n'}^{\text{virt}}P_{nl}(r_1)P_{n'l}(r_2)\frac{\left\langle P_{nl}P_{n'l}\left|\frac{r_<^k}{r_>^{k+1}}\right|P_{1s}P_{1s}\right\rangle}{2\varepsilon_{1s}-\varepsilon_{nl}-\varepsilon_{n'l}} \times(-1)^k\langle k\|C^k\|0\rangle^2 \ , \tag{12}$$

where we have used the partial-wave expansion of the Coulomb interaction.[4] Successively better approximations of ρ^k can then be obtained using the full rhs of Eq. (7) with the latest approximation of η given by Eq. (9).

It is well known that it is not an easy task to solve an inhomogeneous partial-differential equation. Numerical instabilities can occur due to contamination by homogeneous solutions. On the contrary, the method using a direct summation over a basis set does not suffer from such difficulties. This method is also more flexible since we have the spectrum explicitly. For these reasons we have chosen to develop the second method, which also turns out to require less computing time. The main problem is to generate a suitable basis set. If we choose to represent all the radial functions on a finite number of discrete radial lattice points, a finite basis set can be obtained which is complete on this discretized space.

III. NUMERICAL METHODS

A. Discrete finite spectrum

Usually when working with numerical basis sets one generates a finite number of bound-state orbitals and represents the continuum with a finite number of continuum orbitals by choosing a mesh in k space. This has two disadvantages. Since one cannot generate all basis orbitals, the basis set is incomplete. Such a basis set also tries to describe the full space, which is quite unnecessary for an atomic bound state. There are also problems in performing radial integrals involving two continuum orbitals, since these integrals can converge very slowly as a function of the cutoff radius if the energies of the two continuum orbitals are close.

An alternative way to view the problem is to consider the atom put in the center of a spherical box, large enough not to disturb the atomic bound-state wave function. Discretizing the radial coordinate inside the sphere, by choosing a lattice of N radial points, one can generate a basis set, with N basis orbitals, which is complete on this discretized space. It is preferable to have the basis set composed of orthogonal orbitals, which is guaranteed if the discretization leads to a symmetric eigenvalue problem.

The radial Schrödinger equation which generates the basis set orbitals is, using atomic units $e=m_e=\hbar=4\pi\epsilon_0=1$,

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}-\frac{Z}{r}\right]P(r)=\varepsilon P(r)\ , \tag{13}$$

which, if discretized on a linear lattice, would yield a symmetric eigenvalue problem. A better description of the atom, however, is obtained by using a logarithmic lattice ($r=e^x$, with a linear lattice in x instead of r). In order to preserve the Hermiticity of the differential operator when discretized, it is necessary to make the transformation

$$P(r)\rightarrow\frac{1}{\sqrt{r}}P(x)\ .$$

With this transformation Eq. (13) becomes

$$\left[-\frac{1}{2}\frac{1}{r}\frac{d^2}{dx^2}\frac{1}{r}+\frac{(l+\frac{1}{2})^2}{2r^2}-\frac{Z}{r}\right]P(x)=\varepsilon P(x)\ , \tag{14}$$

which is possible to discretize in a symmetric manner on the logarithmic lattice. Using the symmetric five-point formula

$$y''(x)=\frac{1}{12h^2}[-y(x-2h)+16y(x-h)-30y(x)+16y(x+h)-y(x+2h)]+O(h^4)$$

(h is the lattice spacing) for the second-order derivative of $y(x)=(1/r)P(x)$ in Eq. (14), leads to the $N\times N$ symmetric eigenvalue problem

$$(A+D)\mathbf{P}=\varepsilon\mathbf{P}\ , \tag{15}$$

where the vector $\mathbf{P}$ is given by

$$\mathbf{P}=(P(x_1),P(x_2),\ldots,P(x_N))\ .$$

The matrix A is diagonal

$$A_{ii}=-\frac{Z}{r_i}+\frac{(l+\frac{1}{2})^2}{2r_i^2},\quad i=1,2,\ldots,N \tag{16}$$

and D is a symmetric band matrix

$$D=-\frac{1}{24h^2}\begin{bmatrix} -\frac{30}{r_1r_1} & \frac{16}{r_1r_2} & -\frac{1}{r_1r_3} & 0 & 0 & \cdots & \cdots \\ \frac{16}{r_2r_1} & -\frac{30}{r_2r_2} & \frac{16}{r_2r_3} & -\frac{1}{r_2r_4} & 0 & 0 & \cdots \\ -\frac{1}{r_3r_1} & \frac{16}{r_3r_2} & -\frac{30}{r_3r_3} & \frac{16}{r_3r_4} & -\frac{1}{r_3r_5} & 0 & \cdots \\ 0 & -\frac{1}{r_4r_2} & \frac{16}{r_4r_3} & -\frac{30}{r_4r_4} & \frac{16}{r_4r_5} & -\frac{1}{r_4r_6} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix}\ .$$

The boundary conditions need special attention. To express the second-order derivative in the first and last few points one needs to know P in a few points outside the N chosen lattice points. Since the sphere is chosen so that the atomic wave function is negligible outside the sphere, it is natural to assume P to be zero beyond the last lattice point. Close to the nucleus (upper left corner of D) P can be approximated by

$$P(r=e^x)\propto r^{l+3/2}\left[1-\frac{Zr}{l+1}\right] \tag{17}$$

for a point nucleus. This formula relates P at the points needed outside the lattice to P at the first few points on the lattice, introducing corrections to the upper left corner of the matrix D. Care has to be taken to maintain the symmetry in making these corrections. This can be achieved by taking

$$P(x_0)=\alpha\left[\frac{P(x_0)}{P(x_1)}\right]P(x_1)+(1-\alpha)\left[\frac{P(x_0)}{P(x_2)}\right]P(x_2)\ ,$$

$$P(x_{-1})=\left[\frac{P(x_{-1})}{P(x_1)}\right]P(x_1)$$

and choosing α appropriately [the ratios are calculated from Eq. (17)].

Now, diagonalization of the symmetric matrix $(A+D)$ leads to N-orthogonal basis-set orbitals and their eigenvalues. It also follows from matrix algebra that this basis set is complete in the sense that any function on our lattice can be described exactly by the basis set. 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 high accuracy is demanded and can be made in a systematic way.

B. Hartree-Fock spectrum

For larger atomic systems the potential from the bare nucleus is a poor approximation, and one has to use either a more general local potential or a nonlocal potential such as the Hartree-Fock (HF) potential in the independent-particle model used as the first approximation of the atomic wave functions. A Hermitian potential consistent with the IPM then has to be used when generating the spectrum. For He we have, in addition to the hydrogenlike potential considered so far, also applied the HF potential. Using the HF potential leads to the following modifications. In Eq. (16), Z is replaced with the effective charge from the direct part of the HF potential

$$Z \rightarrow Z_{\mathrm{dir}}(r_i) \ . \tag{18}$$

The exchange part of the HF potential leads to an additional full matrix V_{ex} in Eq. (15), which for the helium spectrum with angular momentum $l=k$ is

$$(V_{\mathrm{ex}})_{ij} = -\frac{1}{2l+1}\left[\frac{r_<^k}{r_>^k}\right]_{ij} P_{1s}(r_i)P_{1s}(r_j) \ . \tag{19}$$

The function $(r_<^k/r_>^{k+1})_{12}$ has a cusp when $r_1=r_2$, and an ordinary trapezoidal formula would not be very accurate when integrating over such a cusp. By giving different weights to the points close to the cusp, however, we can simulate a more accurate integration formula, as discussed in Sec. III C. Such weights are included in the implementation of Eq. (19), although not explicitly given here.

C. Evaluation of pair functions

In Sec. III A, a five-point formula was used for the second-order derivative when discretizing the Schrödinger equation. This gives an error of order $O(h^4)$, where h is the lattice spacing. To be consistent in evaluating integrals of discretized functions one has to use an interpolation formula leading to an error of the same order. This can be achieved for a smooth function with a symmetric four-point Lagrange polynomial approximating the function between two lattice points. Using the corresponding integration formula to evaluate radial integrals leads to the same result as using the trapezoidal formula (i.e., the same weight on all lattice points) if the function goes to zero fast enough outside the region defined by our lattice, so that the contribution from an imagined continuation of the lattice is negligible. This is true to a good approximation if the first lattice point is chosen close to the nucleus. Being able to use the trapezoidal formula simplifies the evaluation of integrals considerably. It is also important to notice that this is consistent with the properties of our spectrum, which, since it is evaluated from a symmetric matrix, is orthonormal using the trapezoidal formula (ordinary scalar product). Unfortunately this is not true for a function with a cusp like the first-order $\mathcal{R}$, originating from the partial-wave expansion of Eq. (11),

$$\mathcal{R} = \left[\frac{r_<^k}{r_>^{k+1}}\right]_{12} P_{1s}(r_1)P_{1s}(r_2) \ , \tag{20}$$

used to evaluate the first approximation of the radial pair functions. It is possible to remedy this by giving a weight different from one to the points next to the cusp[14] when constructing the rhs. This weight can be chosen so that the simple trapezoidal formula yields an $O(h^4)$ error, the same kind of error as obtained from a four-point Lagrange interpolation polynomial on a smooth function.

In this work we present a new method to treat the cusp. This method is more accurate than the one presented previously,[14] particularly for high partial waves (large k), and can be derived as follows. In contrast to the previous method we consider an integral over both radial coordinates of a function involving a smooth part and the factor $(r_<^k/r_>^{k+1})_{12}$ with the cusp. The smooth part is approximated with symmetrically located interpolation polynomials on the squares between the lattice points, while the cusp factor is treated analytically. Integrating over both radial coordinates then yields the weights for the different lattice points. Formally we get these weights by considering a function which is zero on all lattice points except one and integrating over all squares. For a function without the cusp factor, we would get the same weight on all lattice points, the weight one if the lattice step h is appropriately included in the function. Including the cusp factor we also get the same weight on all points that do not give contributions to the integral on both sides of the cusp. This weight is, however, different from unity and depends on h and k. For the lattice points close to the cusp, giving contributions to the integral on both sides of the cusp, weights also depending on h and k are obtained. These weights come out to be the same on each subdiagonal.

Using four-point Lagrange interpolation polynomials for the smooth part, we thus end up with five weights to be calculated for each h and k, one weight for the diagonal $r_i=r_j$ where the cusp is located, one weight each on the three main subdiagonals, and one weight for the rest of the lattice points. In deriving the different weights we have utilized the properties of a logarithmic grid. Applying these weights to the $\mathcal{R}$, Eq. (20), all integrations can then be done with the simple trapezoidal formula.

The evaluation of the radial pair function of Eq. (12) is now straightforward. For a fixed n the single-particle wave packet formed by summing over n' can be calculated and the corresponding two-particle contribution added to the pair function using approximately $4N^2$ multiplications. Since this has to be done for n running over all the N basis functions, the total number of multiplications to evaluate a pair function is approximately $4N^3$. This result does not depend on using the first-order $\mathcal{R}$ of Eq. (20) but is valid for any (higher-order) radial $\mathcal{R}$ originating from Eq. (7).

The effort to set up the first-order $\mathcal{R}$, Eq. (20), is proportional to N^2 and is negligible compared to the evaluation of the pair function. Evaluating higher-order radial $\mathcal{R}$'s involves integrals over previously calculated radial pair functions. The effort to evaluate these integrals is also proportional to N^2, but since the number of integrals to evaluate increases with the number of radial pair functions used in the calculation, the evaluation of $\mathcal{R}$ will take a substantial amount of the computing time if many pair functions are involved.

IV. RESULTS FOR HELIUM

In this section results from numerical solution of the pair equation Eqs. (7) and (10) are presented. The first-order equation decouples to independent radial equations for the different partial waves with $\mathcal{R}$ given by Eq. (20). From the corresponding first-order radial pair functions, Eq. (12), the contributions to the second-order correlation energy are calculated using Eq. (8).

We have also solved the pair equation to self-consistency. This involves an iterative solution of coupled radial equations, for the different partial waves, using the full rhs of Eq. (7). The corresponding all-order energies are then achieved from Eq. (8).

The equations given in Sec. II were derived considering a hydrogenlike spectrum. In addition to using such a spectrum, we have solved the Schrödinger equation for helium using a Hartree-Fock spectrum. The corresponding equation is more complicated and involves the coupling between single and double excitations.[4]

The range of the lattice used in all calculations 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. Although the discussion in this paper for simplicity reasons involves using a five-point formula for the second-order derivative, our calculations were actually performed using a seven-point formula.

All the calculations reported were performed on a SUN 4/110 work station using a total amount of about 20 h of CPU time. The solution of one pair function in, say, 101 points is, however, only about 10 s. The total amount of computing time involves iterative solution of the pair equation to self-consistency for all the l limits with $l \leq 10$ in the four different lattices used.

A. Second-order results

In Table I we give partial-wave contributions $\Delta E_l^{(2)}$ to the correlation energy using hydrogenlike orbitals and compare with similar results from a B-spline method used by Johnson and Sapirstein.[10] The two calculations are in excellent agreement with each other.

The contributions $\Delta E_l^{(2)}$ are for high l asymptotically given by the Schwartz formula[15,16]

$$\Delta E_l^{(2)}=-\tfrac{45}{256}(l+\tfrac{1}{2})^{-4}[1-\tfrac{5}{4}(l+\tfrac{1}{2})^{-2}+\tfrac{183}{64}(l+\tfrac{1}{2})^{-4} +O(l^{-6})] . \qquad (21)$$

Using this formula, the tail contribution from $l>10$ can be calculated to be

$$\sum_{l=11}^{\infty} \Delta E^{(2)}(l) \approx (4357.5)\times 10^{-8} \text{ a.u.}$$

The $(l+1/2)^{-8}$ term in this sum is almost negligible, contributing a few parts times 10^{-9} a.u. The tail contribution can also be evaluated from our numerical results (the calculated $\Delta E_l^{(2)}$). Making a fit to the last few $\Delta E_l^{(2)}$ with two terms proportional to $(l+1/2)^{-4,-6}$ yields the tail contribution from $l>10$ to $(4357\pm1)\times10^{-8}$ a.u. consistent with the analytical result. Adding this tail contribution we get agreement for the second-order correlation energy to eight decimal places with the very accurate result of Baker *et al.*[17]

TABLE I. Second-order contributions $\Delta E_l^{(2)}$ from different partial waves l to the correlation energy of He. The correlation energy is evaluated relative to the energy -2.75 a.u., the expectation value of Ψ_0 constructed from hydrogenlike orbitals. Energies in atomic units.

	This work		Johnson and Sapirstein[a]
l	$\Delta E_l^{(2)}$	$E_l^{(2)}$	$\Delta E_l^{(2)}$
0	−0.125 333 84	−0.125 333 84	−0.125 333 83
1	−0.026 495 16	−0.151 829 00	−0.026 495 16
2	−0.003 906 13	−0.155 735 13	−0.003 906 13
3	−0.001 077 73	−0.156 812 86	−0.001 077 73
4	−0.000 406 10	−0.157 218 96	−0.000 406 10
5	−0.000 185 00	−0.157 403 96	−0.000 184 99
6	−0.000 095 79	−0.157 499 74	−0.000 095 79
7	−0.000 054 40	−0.157 554 14	−0.000 054 39
8	−0.000 033 12	−0.157 587 26	−0.000 033 12
9	−0.000 021 29	−0.157 608 56	−0.000 021 29
10	−0.000 014 30	−0.157 622 86	−0.000 014 30
$\sum_{l=11}^{\infty}$	−0.000 043 57		−0.000 043 57
$\sum_{l=0}^{\infty}$		−0.157 666 43	−0.157 666 40
Exact		−0.157 666 429 5[b]	

[a] Reference 10.

[b] Reference 17.

TABLE II. All-order correlation energies of He in different partial-wave limits using hydrogenlike orbitals. Correlation energies E_l are given relative to $E_0+E_1=-2.75$ a.u. Energies in atomic units.

	This work		Carroll *et al.*[a]	Mårtensson[b]
l	ΔE_l	E_l	E_l	E_l
0	−0.129 028 77	−0.129 028 77	−0.129 028 765	−0.129 02
1	−0.021 487 48	−0.150 516 25	−0.150 516 220	−0.150 50
2	−0.002 250 61	−0.152 766 85	−0.152 766 822	−0.152 74
3	−0.000 554 23	−0.153 321 09	−0.153 321 079	−0.153 28
4	−0.000 197 52	−0.153 518 60	−0.153 518 598	−0.153 47
5	−0.000 087 11	−0.153 605 72	−0.153 605 71	
6	−0.000 044 18	−0.153 649 89	−0.153 649 88	
7	−0.000 024 73	−0.153 674 62	−0.153 674 59	−0.153 60
8	−0.000 014 90	−0.153 689 52	−0.153 689 47	
9	−0.000 009 50	−0.153 699 02	−0.153 698 95	
10	−0.000 006 35	−0.153 705 37	−0.153 705 27	
$\sum_{l=11}^{\infty}$	−0.000 019 02[c]			
$\sum_{l=0}^{\infty}$		−0.153 724 39	−0.153 724 3	
Exact		−0.153 724 377 034[d]		

[a] Reference 18.
[b] Reference 8.
[c] Using C_3 and C_4 from Eq. (26) and our estimated C_5, as described in Sec. IV B.
[d] Reference 12.

B. All-order results

The partial-wave expansion of the pair function is given in Eq. (9). When solving the pair equation to self-consistency, we have to truncate this expansion after some $k=l$. The truncated solution then gives, through Eq. (8), the partial-wave limits E_l of the correlation energy. Our calculated E_l are presented in Table II. We claim our partial-wave limits to be accurate to a few parts in 10^8. In Table II we also compare with results previously obtained in our group using a different method,[8] and with results by Carroll *et al.*[18]

In the method previously used in our group the radial differential equations originating from Eq. (7) were solved directly with a numerical method. Comparison with the present calculation shows a substantial improvement in accuracy. This has mainly two sources: the improved treatment of the cusp and the use of more dense lattices. In Table III our results for the different lattices used are presented to show the magnitude of extrapolation due to finite lattice effects. Although we have used a seven-point formula for the second-order derivative giving an $O(h^6)$ error in our spectrum, we have found the dependence on lattice spacing for correlation energies to behave as

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

This we attribute to higher-order effects of the cusp in the

TABLE III. All-order correlation energies, using hydrogenlike orbitals, for different number of points N in the lattice, and the corresponding results extrapolated to zero spacing. The two figures after the decimal point are only significant for describing differences between the different lattices. Energies in atomic units (10^{-8} a.u.).

l	$N=85$	$N=91$	$N=101$	$N=121$	Extrapolated
0	−12 902 869.31	−12 902 871.36	−12 902 873.45	−12 902 875.33	−12 902 876.74
1	−2 148 735.00	−2 148 738.58	−2 148 742.25	−2 148 745.58	−2 148 748.13
2	−225 044.02	−225 048.43	−225 053.04	−225 057.30	−225 060.53
3	−55 404.98	−55 409.69	−55 414.69	−55 419.44	−55 423.35
4	−19 732.59	−19 737.32	−19 742.43	−19 747.41	−19 751.73
5	−8691.94	−8696.51	−8701.53	−8706.55	−8711.19
6	−4398.79	−4403.08	−4407.88	−4412.80	−4417.54
7	−2454.80	−2458.76	−2463.27	−2467.99	−2472.68
8	−1472.96	−1476.55	−1480.71	−1485.19	−1489.96
9	−934.55	−937.79	−941.60	−945.77	−950.30
10	−619.78	−622.66	−626.10	−629.98	−634.54
$\sum_{l=0}^{10}$	−15 370 358.72	−15 370 400.73	−15 370 446.95	−15 370 493.34	−15 370 536.69

TABLE IV. Coefficients in the asymptotic formula for ΔE_l [Eq. (22)] determined from three consecutive partial-wave limits using a different maximum l. The resulting tail contributions (10^{-8} a.u.) for $l > 10$ are also given.

l	D_4	D_5	$\sum_{l=11}^{\infty}$
2,3,4	-0.0716	-0.0409	-1854
5,6,7	-0.0742	-0.0305	-1901
8,9,10	-0.0743	-0.0294	-1903

pair functions. We have used four different lattices with 85, 91, 101, and 121 points, respectively. Using a single lattice with, say, 91 points, the error due to the finite lattice 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.

The results by Carroll *et al.* given in Table II were achieved by a CI calculation analyzed in terms of natural orbitals. Comparing with their result, extrapolated in the number of natural orbitals, we find good agreement except for the higher l limits. We believe that our high l-limit results are the more accurate ones.

Including partial waves up to $l=10$ gives the total correlation energy accurate to two parts in 10^5 (see Table II). 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 to increase the accuracy. This extrapolation is the main limitation of the accuracy for two-electron systems.

For the all-order results the asymptotic formula for ΔE_l includes also odd powers of $(l+1/2)$ in contrast to Eq. (21) (Ref. 18)

$$\Delta E_l = D_4(l+\tfrac{1}{2})^{-4} + D_5(l+\tfrac{1}{2})^{-5} + D_6(l+\tfrac{1}{2})^{-6} + O(l^{-7}) \ . \qquad (22)$$

The D_n coefficients can be estimated by a fit to our calculated ΔE_l. We have found numerical problems determining accurately more than the first two D_n coefficients by such a fit. Neglecting the D_6 term we achieve the results given in Table IV. Adding the tail contribution from Table IV achieved with $l_{\max}=10$, we get the total correlation energy within a few parts in 10^8 (Table II). The corresponding result using $l_{\max}=5$ gives an error of about 4×10^{-7} a.u. The D_4 and D_5 coefficients can also be calculated as an integral over the wave function. This has been done by Hill[19] giving

$$D_4 \approx -0.074\,225\,7, \quad D_5 \approx -0.030\,989\,1 \ . \qquad (23)$$

As can be seen from Table IV, our estimated values are in good agreement with these values.

To explore further the accuracy of our l limits we can look at the difference between our l limits and the extremely accurate calculation by Freund *et al.*[12] This difference is given by the asymptotic formula[19]

$$E_l - E = C_3(l+1)^{-3} + C_4(l+1)^{-4} + C_5(l+1)^{-5} + O(l^{-6}) \ . \qquad (24)$$

The connection with the formula for ΔE_l [Eq. (22)] is

$$D_4 = -3C_3, \quad D_5 = -4C_4, \quad D_6 = -5(\tfrac{1}{2}C_3 + C_5) \ , \qquad (25)$$

which gives

$$C_3 \approx 0.024\,741\,9, \quad C_4 \approx 0.007\,747\,27 \ . \qquad (26)$$

In Table V we give the contribution from the C_3 and C_4 terms of Eq. (24) for different l, and the contribution from the remaining terms deduced using our calculated l limits. For large l the C_5 term should dominate this remainder. In Fig. 1, a log-log plot of the remainder is given. The slope of the curve in Fig. 1 is approximately -4.7, indicating that we have the expected $(l+1)^{-5}$ dependence. Assuming this dependence the coefficient C_5 can be estimated, by a least-squares fit, $C_5 \approx -0.015$. One would have expected the slope to come closer to -5 going to larger l but we see a tendency for the opposite. This artifact can be explained if we assume an error of about two parts in 10^8 for our higher l limits. With our estimated coefficient C_5 we get the tail contribution from $l > 10$ to -1902×10^{-8} a.u. (Table II) giving the total energy of helium to $-2.903\,724\,39$ a.u. It is interesting to

TABLE V. Examination of the $(l+1)^{-5}$ dependence in Eq. (24) using our all-order partial-wave limits for He. Energies in atomic units (10^{-8} a.u.).

l	E_l	$A_3(l)$ $-C_3(l+1)^{-3}$ [a]	$A_4(l)$ $-C_4(l+1)^{-4}$ [a]	$A_5(l)+\cdots$ $[E_\infty-(E_l+A_3+A_4)]$ [b]
4	$-153\,518\,60.5$	$-19\,793.52$	-1239.56	455.9
5	$-153\,605\,71.7$	$-11\,454.58$	-597.78	186.3
6	$-153\,649\,89.2$	-7213.38	-322.67	87.6
7	$-153\,674\,61.9$	-4832.40	-189.14	45.7
8	$-153\,689\,51.8$	-3393.95	-118.08	26.2
9	$-153\,699\,02.1$	-2474.19	-77.47	16.1
10	$-153\,705\,36.7$	-1858.90	-52.91	10.8

[a] From Ref. 17; $C_3 \approx 0.024\,741\,9$ and $C_4 \approx 0.007\,747\,27$.

[b] Using $E_\infty = -0.153\,724\,377\,034$ from Ref. 12.

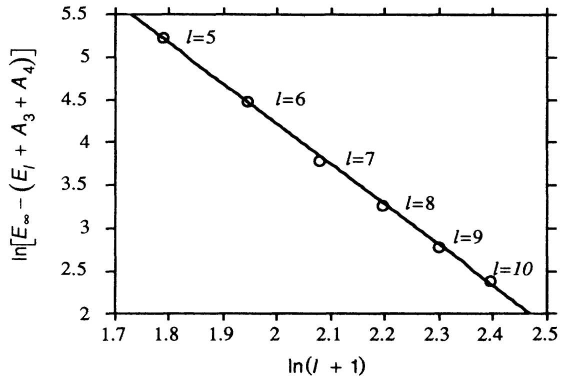

FIG. 1. Log-log plot of the residual energy from the last column of Table V as a function of $(l+1)$. Assuming an $(l+1)^{-\alpha}$ dependence, α can be determined as the slope of the curve giving $\alpha \approx 4.7$.

note that the coefficient D_6 in Eqs. (22), (23), and (25) fortuitously is quite small due to cancellation

$$D_6 = -5(\tfrac{1}{2}C_3 + C_5) \approx -5(0.012\,371 - 0.015)$$
$$\approx 0.013\ , \qquad (27)$$

where the last figure is very uncertain. The contribution to the $l > 10$ tail from the D_6 term in Eq. (22) is thus only about two parts in 10^8, explaining the accurate result using only the D_4 and D_5 terms in the fit (Table IV). Compare this with the contribution from the C_5 term of Eq. (24) giving a contribution of about one part in 10^7 to the $l > 10$ tail.

The discussion above shows that the slow l convergence is a problem if high accuracy is wanted. The reason for the slow convergence is the cusp in the wave function when $\mathbf{r}_1 = \mathbf{r}_2$. Promising attempts have been made by Kutzelnigg[20] to include the correct cusp behavior in the wave function by making the ansatz

$$\Psi = (1 + \tfrac{1}{2} r_{12})\Phi$$

and expand Φ in partial waves. Already by approximating Φ with $|1s^2\rangle$, using a hydrogenlike $1s$ orbital, he achieves the approximate D_n coefficients [Eq. (22)] $D_4 \approx -0.071$, $D_5 \approx -0.029$, and $D_6 \approx 0.016$, which are quite close to the accurate values of D_4 and D_5 [Eq. (23)], given by Hill, and our estimated value for D_6 [Eq. (27)].

C. Hartree-Fock results

We have developed a general computer code based on the coupled-cluster method including all effects of single and double excitations.[5] We have implemented our new method to calculate pair functions into this code that can treat a general potential. Results using the HF spectrum, discussed in Sec. III B, are presented in Table VI. All the partial-wave contributions ΔE_l should be the same as the corresponding ones (see Table II) using hydrogenlike orbitals, except the $l = 0$ contribution, which is affected by which $|1s^2\rangle$ zeroth-order wave function is used. In principle, we should expect the same accuracy in the two calculations. In the HF calculation, however, we need a $1s$ HF orbital as input to the code to build the HF potential, Eqs. (18) and (19), and we introduce a small error (about one part in 10^7 for the correlation energy) when interpolating this orbital to the lattice used. The very good agreement with the results using hydrogenlike orbitals shows that the code treats correctly the coupling between the single and double excitations occurring using the HF potential.

V. CONCLUSION

We have described a method for the solution of the pair equation based on summation over a finite spectrum. This spectrum is obtained by diagonalization of the discretized one-particle Schrödinger Hamiltonian. We have succeeded in discretizing the Hamiltonian without destroying the Hermiticity. Generating the spectrum in this way leads automatically to an orthogonal and complete spectrum which is very suitable for the use in perturbation theory when studying many-electron atoms.

TABLE VI. All-order correlation energies of He in different partial-wave limits using HF orbitals. Correlation energies E_l are given relative to $E_{\mathrm{HF}} = -2.861\,680\,0$. Energies in atomic units.

l	ΔE_l	E_l	$E_{\mathrm{HF}} + E_l$	E_H[a]
0	−0.017 348 7	−0.017 348 7	−2.879 028 7	−2.879 028 77
1	−0.021 487 4	−0.038 836 2	−2.900 516 2	−2.900 516 25
2	−0.002 250 6	−0.041 086 8	−2.902 766 8	−2.902 766 85
3	−0.000 554 2	−0.041 641 0	−2.903 321 0	−2.903 321 09
4	−0.000 197 5	−0.041 838 5	−2.903 518 5	−2.903 518 60
5	−0.000 087 1	−0.041 925 6	−2.903 605 6	−2.903 605 72
6	−0.000 044 2	−0.041 969 8	−2.903 649 8	−2.903 649 89
7	−0.000 024 7	−0.041 994 5	−2.903 674 5	−2.903 674 62
8	−0.000 014 9	−0.042 009 4	−2.903 689 4	−2.903 689 52
9	−0.000 009 5	−0.042 018 9	−2.903 698 9	−2.903 699 02
10	−0.000 006 3	−0.042 025 3	−2.903 705 3	−2.903 705 37

[a] Total energies $E_H = E_0 + E_1 + E_l$, using hydrogenlike orbitals, deduced from Table II.

It is possible to implement the method so that an N^3 dependence for the number of operations needed to evaluate a radial pair function is achieved, where N is the number of lattice points used. An accuracy of one part in 10^7 is easily obtained for helium and can be further improved by increasing the number of lattice points. This numerical accuracy, achieved for helium, promises that the method will be sufficiently accurate applied to heavier atoms with many electrons, for which we expect to lose some accuracy due to the increased number of nodes in the wave function. The numerical error will be negligible compared to omitted many-body effects in most applications.

The method presented can easily, with some modifications, also be applied to the relativistic case where it seems to be even more promising. A great advantage there is that the method yields explicitly the positive and negative spectrum and thus no explicit energy projection operators are needed. The effect of such projection operators is trivially obtained by restrictions in the summations.

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