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Relativistic all-order equations for helium

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The ground-state energy of helium is calculated to all orders in perturbation theory starting from a relativistic "no-pair" many-body Hamiltonian in which contributions of virtual electron-positron pairs are ignored. In this calculation only Coulomb interactions between the electrons are considered. Two all-order calculations are presented: one calculation is based on nuclear Coulomb-field orbitals and the second is based on Hartree-Fock orbitals. For each calculation the all-order equations of many-body perturbation theory are solved iteratively. The resulting numerical value for the ground-state energy from the Coulomb-field calculation is $-2.903\,856(1)$ a.u., while the Hartree-Fock calculation gives $-2.903\,855(2)$ a.u. Both of these values agree with that obtained by correcting the well-established nonrelativistic energy for lowest-order relativistic effects.

INTRODUCTION

Many-body perturbation theory (MBPT), introduced into atomic physics by Kelly,[1] provides a powerful and systematic approach to the calculation of atomic properties. In MBPT, one introduces a central potential $U(r)$, which is in principle arbitrary, though in practice is most often chosen to be the Hartree-Fock potential. One uses this potential to determine a set of single-particle orbitals. In the lowest order of perturbation theory, the atomic state is a Slater determinant formed from these orbitals and the total energy is the sum of the orbital energies. The difference between the actual electron-electron interaction and the central potential $U(r)$ is the perturbing Hamiltonian. Consideration of this perturbing interaction in higher orders leads to the formulas of MBPT. In practice, these formulas become so complicated that direct perturbative studies are rarely carried out beyond second order. Instead, higher-order corrections are treated by so-called all-order methods in which infinite subclasses of contributions are summed. It is our aim to set up a relativistic all-order formalism for use on heavy atoms such as cesium or thallium, which are of great current interest because of the recent accurate measurements of parity nonconserving electric dipole amplitudes.[2] As a first step towards this goal, we consider here the application of all-order methods to the ground state of helium.

Generally, all-order methods fail to account for all terms of a given order in the perturbation expansion. In the special case of the ground state of the helium atom, however, the presence of only two electrons allows one to formulate and solve exact all-order equations. We treat the ground state in two different ways; one treatment is based on nuclear Coulomb-field orbitals and the second treatment is based on Hartree-Fock (HF) orbitals. Both calculations are relativistic; they may be considered as extensions of recent all-order work by Lindroth.[3] The results of the present calculations can be compared with the highly accurate calculations of the nonrelativistic ground-state energy of helium corrected to order $(Z\alpha)^2$ a.u. for relativistic effects.[4] Such a comparison provides a stringent test of the numerical methods used in the present approach to the many-body problem. We find that our methods are powerful enough to recover seven digits of the ground-state energy for neutral helium; several more digits could be added if desired. We stress that the most accurate calculations so far carried out on this state are the nonrelativistic variational calculations mentioned above. The purpose of this work is to show that all-order methods can also be highly accurate; moreover, all-order methods can be formulated to account for relativistic effects automatically. Furthermore, although variational techniques work very well for two-electron systems, the all-order approach described here can in principle be applied to more complicated atoms. In the terminology of Lindgren and Morrison,[5] the approach described here generalizes to the *pair approximation,* in which effects associated with single and double excitations from the core are summed to all orders in perturbation theory. While no work has been done on atoms as large as cesium or thallium, there is considerable evidence from nonrelativistic calculations on smaller atoms and molecules that terms omitted in this approximation are a small fraction of the total correlation. For example, Bunge[6] finds for Be that triple excitations constitute 1.1% of correlation, while quadruple excitations (dominated by *coupled-cluster* terms) constitute 3.4% of correlation. If these terms in cesium and thallium are also relatively small, it should be possible to account for them to sufficient accuracy using only low orders of perturbation theory (coupled cluster terms can also be incorporated in the pair approximation and iterated to higher order if necessary), and the use of all-order methods may then provide the best way to treat the structure of many-electron atoms.

Before turning to a description of the calculation, we note the present treatment of the energy is incomplete in several respects. Specifically, we neglect finite nuclear size effects, mass polarization and reduced mass effects, radiative corrections, and finally we neglect the Breit interaction; each of these terms can be treated as perturbations later, if desired. With these approximations, the ground-state energy is known to be $-2.903\,856\,49$ a.u. We obtain this value by adding to the highly accurate nonrelativistic energy,[4] $E_{\text{nonrel}}=-2.903\,724\,38$ a.u., those relativistic corrections of order $(Z\alpha)^2$ not associated with the Breit interaction,[4] $\Delta E_{\text{rel}}=-0.000\,132\,11$ a.u., where ΔE_{rel} is the electrostatic energy. Our calculations should in fact be expected to deviate from this value after some number of digits since our calculations also include higher-order relativistic effects starting with corrections of order $(Z\alpha)^4$ a.u. For neutral helium, however, these higher-order relativistic corrections are very small; indeed they are below the level of sensitivity of the present calculations. Therefore, in the subsequent discussion, we shall for simplicity ignore the fact that our approach implicitly contains contributions of higher order than $(Z\alpha)^2$ a.u. For the calculation based on Coulomb-field orbitals, the lowest-order energy is $-4.000\,213\,03$ a.u., and the first-order energy is $1.250\,098\,06$ a.u.[7] Thus in the present calculation we should expect to obtain $-0.153\,741\,53$ a.u. for the Coulomb-field correlation energy (we shall use the term *correlation energy* to refer to all corrections of second and higher order in whatever perturbation series is under discussion). For the calculation based on Hartree-Fock orbitals the HF energy is $-2.861\,813\,34$ a.u., so that here the correlation energy is expected to be $-0.042\,043\,15$ a.u.

Since one novel feature of the present work is the combination of relativity with correlation, it is of interest to examine what fraction of these correlation energies are relativistic in origin. We summarize the situation in Table I, where the nonrelativistic MBPT energies are given together with the corresponding (electrostatic) relativistic contributions for both potentials. From this table we see how the order $(Z\alpha)^2$ a.u. relativistic correction mentioned above is apportioned between the correlation energy and the zeroth and first-order energy for each potential. It should be borne in mind that the numerical accuracy of the present calculation is of order 1 or 2 in the sixth decimal place. Thus, while there is a detectable relativistic contribution of $-0.000\,017$ a.u. to the Coulomb-field correlation energy, the relativistic contribution to the HF correlation energy is just below the limit of detectability at the present level of precision.

Our point of departure for the development of the all-order treatment of the ground-state of helium is the relativistic "no-pair" Hamiltonian

$$H=H_0+V_I\ , \tag{1}$$

$$H_0=\sum_i h_i\ , \tag{2}$$

$$h=c\boldsymbol{\alpha}\cdot\mathbf{p}+(\beta-1)c^2+V_{\text{nuc}}(r)+U(r)\ , \tag{3}$$

$$V_I=\sum_{\substack{i,j\\ i>j}}\Lambda_{++}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\Lambda_{++}-\sum_i\Lambda_{+}U(r_i)\Lambda_{+}\ . \tag{4}$$

In Eq. (3), $U(r)$ is the central potential introduced in the model Hamiltonian H_0 to account approximately for the electron-electron interaction. This potential is subtracted out again from the interaction potential V_I in Eq. (4). The positive energy projection operators Λ_{++} and Λ_{+} in Eq. (4) refer to states calculated in the potential $U(r)$. These projection operators are introduced to avoid the well-known difficulty of continuum dissolution[8] associated with relativistic many-body calculations. Negative energy states do play a role in calculations of the energy shift, but contributions from negative energy states enter in order α^3 a.u.; they are associated with the Lamb shift, and can be treated separately.

For the first of our two calculations we choose $U(r)=0$ and base our calculations on Dirac-Coulomb orbitals. In the second calculation we choose $U(r)=V_{\text{HF}}(r)$, the Dirac-Hartree-Fock potential,

$$\langle i|V_{\text{HF}}|j\rangle\equiv\sum_a\tilde{g}_{aiaj}\ . \tag{5}$$

In Eq. (5) and later we adopt the convention that the letters at the first part of the alphabet, $a,b,c,\ldots,$ represent occupied core states; those near the middle of

TABLE I. Comparison of nonrelativistic MBPT contributions with the corresponding relativistic electrostatic contributions. All values are in a.u. Note that (i) the correlation energies given are *deduced* by subtracting the lower-order contributions from the total, (ii) the totals are taken from the sources given in the Introduction, and that (iii) in obtaining the total relativistic energy, we have disregarded contributions of order $(Z\alpha)^4$ a.u. and higher, which are in principle included in relativistic MBPT.

	E_{rel}	E_{nonrel}	$E_{\text{rel}}-E_{\text{nonrel}}$
	Coulomb potential		
Zeroth order	−4.000 213 03	−4.000 000 00	−0.000 213 03
First order	1.250 098 06	1.250 000 00	0.000 098 06
Correlation	−0.153 741 52	−0.153 724 38	−0.000 017 14
Total	−2.903 856 49	−2.903 724 38	−0.000 132 11
	Hartree-Fock potential		
HF energy	−2.861 813 34	−2.861 679 99	−0.000 133 35
Correlation	−0.042 043 15	−0.042 044 39	0.000 001 24
Total	−2.903 856 49	−2.903 724 38	−0.000 132 11

the alphabet, $i,j,k,\dots$, designate arbitrary states; while those later in the alphabet, $r,s,t,\dots$, represent unoccupied excited states. The quantity $\tilde{g}_{ijkl} \equiv g_{ijkl} - g_{ijlk}$, where the Coulomb matrix element g_{ijkl} is given by

$$g_{ijkl} = \int \int d^3r\, d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|} u_i^\dagger(\mathbf{r}) u_k(\mathbf{r}) \times u_j^\dagger(\mathbf{r}') u_l(\mathbf{r}') , \tag{6}$$

and $u_i(\mathbf{r})$ is a single-particle orbital.

COULOMB POTENTIAL CALCULATION

The first method we describe is based on orbitals determined in the nuclear Coulomb potential with $U(r)=0$. The corrections to the ground-state energy from the lowest four orders of MBPT are shown in Table II. It is noteworthy that for this particularly simple system the convergence of perturbation theory is relatively rapid, so that at fourth order there is agreement with the known result at the 10-ppm level.

To organize the perturbation expansion so that all orders can be accounted for, we write

$$|\Psi\rangle = N(|0_C\rangle + |2_C\rangle) , \tag{7}$$

where

$$|0_C\rangle = a^\dagger_{1s\uparrow} a^\dagger_{1s\downarrow} |0\rangle \tag{8a}$$

and

$$|2_C\rangle = \sum_{a,b,i,j}{}' \rho_{ijab} a_i^\dagger a_j^\dagger a_a a_b |0_C\rangle . \tag{8b}$$

The operators $a^\dagger$ and a refer to the creation and destruction of Dirac-Coulomb states, N is a normalization factor, and $|0\rangle$ is the vacuum, so that $|0_C\rangle$ describes a rather inaccurate starting wave function, with binding energy $E_0 = 2\epsilon_{1s} = -4.000\,213\,03$ a.u. This inaccuracy is remedied by including $|2_C\rangle$. We use a notation appropriate to a general closed shell system; in our case the sum over a and b ranges over only $1s\uparrow$ and $1s\downarrow$. Thus the destruction operators empty the core, which is then repopulated with states i and j, with the exception that i and j cannot both be $1s$ states; that is the meaning of the prime in Eq. (8b).

TABLE II. Low-order corrections to the ground-state energy of helium from many-body perturbation theory from calculations based on Coulomb orbitals and for calculations based on Hartree-Fock orbitals (in units of a.u.).

Term	Coulomb	Hartree-Fock
E_0	−4.000 21	−1.835 98
E_1	1.250 10	−1.025 83
E_2	−0.157 68	−0.037 37
E_3	0.004 34 (NR)[a]	−0.003 77 (NR)
E_4	−0.000 21 (NR)	−0.000 85 (NR)
E_{sum}	−2.903 66	−2.903 80

[a] The nonrelativistic (NR) values are taken from Ref. 12.

For a general atom, Eq. (7) would be incomplete since one could, for example, include a wave function correction $|3_C\rangle$, in which three destruction operators were followed by three creation operators. However, since $|0_C\rangle$ for helium contains only two electrons, all such terms vanish in the case considered here and this representation is complete. If we define $E \equiv E_0 + \Delta E$, then $(H_0 + V_I)|\Psi\rangle = E|\Psi\rangle$ reduces to the following set of equations:

$$(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)\rho_{ijab} = \tfrac{1}{2}g_{ijab} - \sum_{kl}{}' g_{ijkl}\rho_{klab} + \Delta E \rho_{ijab} , \tag{9}$$

$$\Delta E = \tfrac{1}{2} \sum_{a,b} \tilde{g}_{abab} - \sum_{a,b,i,j}{}' \rho_{ijab} \tilde{g}_{abij} . \tag{10}$$

It is convenient to rewrite the Coulomb matrix elements in terms of Slater-type integrals. To this end we set

$$g_{ijkl} = \sum_{L=0}^{\infty} X_L(ijkl) J_L(ijkl) , \tag{11}$$

where

$$J_L(ijkl) = \sum_M (-1)^{j_i + j_j + L + m_i + m_j + M} \times \begin{bmatrix} L & j_k & j_i \\ M & m_k & -m_i \end{bmatrix} \begin{bmatrix} L & j_j & j_l \\ M & m_j & -m_l \end{bmatrix} \tag{12a}$$

and

$$X_L(ijkl) = (-1)^L C_L(ik) C_L(jl) R_L(ijkl) . \tag{12b}$$

In Eq. (12b) we have introduced the angular factors C_L and the Slater integrals R_L which are defined by

$$C_L(ij) = (-1)^{j_i + 1/2} \sqrt{(2j_i+1)} \sqrt{(2j_j+1)} \times \begin{bmatrix} L & j_i & j_j \\ 0 & -\frac{1}{2} & \frac{1}{2} \end{bmatrix} \Pi(l_i, l_j, L) , \tag{13a}$$

$$R_L(ijkl) = \int \int dr\, dr' r_<^L / r_>^{L+1} [g_i(r) g_k(r) + f_i(r) f_k(r)] \times [g_j(r') g_l(r') + f_j(r') f_l(r')] , \tag{13b}$$

TABLE III. Partial-wave contributions to the all-order Coulomb-field correlation energy (in units of a.u.).

L	ΔE	$\Delta E(L)$
0	−0.129 049 6	−0.129 049 6
1	−0.151 423 9	−0.022 374 3(1)
2	−0.153 079 6	−0.001 655 7(1)
3	−0.153 461 1	−0.000 381 5(2)
4	−0.153 595 4	−0.000 134 4(2)
5	−0.153 655 5	−0.000 060 1(1)
6	−0.153 686 5	−0.000 031 0(1)
∞	−0.153 741(1)	

where Π equals 1 if the sum of its three arguments is even and zero if the sum is odd. The functions $g(r)$ and $f(r)$ are the upper and lower components of the radial Dirac wave functions. In order for $|\Psi\rangle$ to have the same angular momentum as $|0_C\rangle$, it is necessary that ρ has an angular momentum expansion of the same form as that of g. We may therefore write

$$\rho_{ijab}=\sum_{L=0}^{\infty} S_L(ijab)J_L(ijab)\ . \tag{14}$$

Substituting Eq. (14) into the basic equation, Eq. (9), and making use of the JLV4 theorem (Jucys-Levinson-Vanagus theorem 4, as defined by Lindgren and Morrison[5]) we find

$$S_L(ijab)=\frac{1}{2(\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b)}X_L(ijab)-\tfrac{1}{2}\sum_{l_1,l_2}\sum_{k,l}(2L+1)(-1)^{j_a+j_b+j_i+j_j}\begin{Bmatrix} j_b & j_j & L\\ l_1 & l_2 & j_l\end{Bmatrix}\begin{Bmatrix} j_a & j_i & L\\ l_1 & l_2 & j_k\end{Bmatrix}$$
$$\times\frac{X_{l_1}(ijkl)S_{l_2}(klab)}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b}+\frac{\Delta E}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b}S_L(ijab)\ . \tag{15}$$

While it would be possible to absorb the last term by rearranging the denominators, it was found that doing so caused the iterative scheme to diverge. The divergence can be traced to the large value of ΔE. The numerical method used to solve this set of coupled equations was based on the use of the finite basis sets described in Ref. 9. Thirty-five positive energy states were generated from piecewise quartic polynomials. The basis set was chosen to reproduce the highly accurate second-order calculation[7] with an error of less than 10^{-6} a.u., which was the accuracy chosen for this application. The last ten states for s, p, and d orbitals, and the last five for f and higher orbitals were not summed over, as this approximation affected the result only in order 10^{-8} a.u. Equation (15) was then solved iteratively until the seventh digit past the decimal place was stable. The iteration solution required on the order of ten passes. This procedure was carried out for angular momentum cutoffs from 0 to 6. The same cutoff was applied to all angular momenta in the problem, namely, L, l_1, and l_2, with all j values allowed by the triangle relation included. The resulting values of ΔE are presented in Table III. The calculations were performed on a CRAY XMP/48, and took about three cpu hours.

We note that the $L=0$ result is in excellent agreement with the calculation of Lindroth,[3] which involved the use of very different numerical techniques. To extrapolate the cutoff angular momentum to infinity, the change in ΔE from adding one more partial wave is tabulated in the second column of Table II. This change for $L=3$, 4, 5, and 6 is then fitted to an expression of the form $A/L^4+B/L^5+C/L^6$. This form was chosen because it reproduces with very high accuracy the $L=7$, 8, 9, and 10 partial waves when used in the same way for the partial wave expansion of the second order energy.[7] If A, B, and C are fitted with the $L=3$, 4, and 5 data, and the sum carried out to $L=1000$, one finds $\Delta E(3,4,5)=-0.153\,740\,2$ a.u. If instead the $L=4$, 5, and 6 result are used, then $\Delta E(4,5,6)=-0.153\,740\,9$ a.u. Adding in a term D/L^7 gives finally $\Delta E(3,4,5,6)=-0.153\,741\,0$ a.u. From these values together with an estimated basis set truncation error, we assign an overall estimate of one in the sixth digit past the decimal place, and quote as the final answer for the Coulomb-field calculation

$$E_{\text{Coulomb}}=-2.903\,856(1)\ \text{a.u.}\ , \tag{16}$$

in agreement with the expected result.

TABLE IV. Alternative partial-wave contributions to the all-order Coulomb field correlation energy compared with the nonrelativistic results of Ref. 10 (in units of a.u.).

L	E_{rel}	E_{nonrel}
0	$-2.879\,165$	$-2.879\,029$
1	$-2.900\,650$	$-2.900\,516$
2	$-2.902\,901$	$-2.902\,767$

The method of cutting off the angular momentum described above is not unique, and in fact it is more common not to restrict the summations over L, l_1, and l_2, restricting instead only the angular momenta of the intermediate states. In order to compare with previous nonrelativistic work[10] we have used this second cutoff for $L_{\max}=0$, 1, and 2. This cutoff was also used for the following HF calculation; it is described in more detail in that discussion. The relativistic and nonrelativistic results are compared in Table IV. The results are in close agreement, with the difference being consistent with the expected relativistic effects.

CALCULATION BASED ON HARTREE-FOCK ORBITALS

In the second calculation we choose $U(r)=V_{\text{HF}}$ and put the interaction Hamiltonian in normal order,

$$V_I=V_0+V_2\ , \tag{17}$$

$$V_0=\tfrac{1}{2}\sum_{ab}\tilde{g}_{abab}\ , \tag{18a}$$

$$V_2=\tfrac{1}{2}\sum_{i,j,k,l} g_{ijkl}{:}a_i^\dagger a_j^\dagger a_l a_k{:}\ , \tag{18b}$$

where the operators inside the colons (: :) are arranged in normal order with respect to the core, so that core creation operators and excited state annihilation operators lie to the right of core annihilation and excited state creation operators. For the Hartree-Fock potential, the interaction Hamiltonian has a zero-body part V_0, which is just the first-order energy shift, and a two-body part

V_2, but no one-body part. Owing to the positive energy projection operators in Eq. (4), the sums over excited states i, j, k, and l are restricted to positive energy states only.

To obtain all-order equations, we write the no-pair wave function as

$$|\Psi\rangle = N\left[1+\sum_{r,a}\rho_{ra}a_r^\dagger a_a+\tfrac{1}{2}\sum_{r,s,a,b}\rho_{rsab}a_r^\dagger a_s^\dagger a_b a_a\right]|0_C\rangle\ , \tag{19}$$

where N is a normalizing factor and $|0_C\rangle$ is the $1s^2$ ground state, now formed from Hartree-Fock orbitals and having total zeroth-order energy $2\epsilon_{1s} = -1.835\,981\,37$ a.u. By writing the wave function in this way, we consider all possible single and double excitations out of the core, and thereby ensure a complete treatment of helium within the context of the no-pair approximation. However, with only a slight modification, the equations we derive will also be useful for a general closed-shell atom; we shall thus keep the indices a and b for core states completely general.

One readily finds for the total energy of the atom,

$$E = \langle 0_C|H_0+V_I|\Psi\rangle/N$$

$$= E^{(0)}+E^{(1)}+\delta E\ , \tag{20}$$

$$E^{(0)} = 2\epsilon_{1s}\ , \tag{21a}$$

$$E^{(1)} = V_0\ , \tag{21b}$$

$$\delta E = \tfrac{1}{2}\sum_{a,b,r,s} g_{abrs}\tilde{\rho}_{rsab}\ , \tag{21c}$$

where V_0 is given by Eq. (18a). The sum of the zero- and first-order energies is just the Hartree-Fock energy, and for helium has the value $E_{\rm HF} = -2.861\,813\,3$ a.u. The remaining contribution δE is the correlation energy, equal to the sum of all second- and higher-order contributions to the energy. The no-pair equation can now be written as

$$(E_0+\delta E-H_0)|\Psi\rangle = V_2|\Psi\rangle\ . \tag{22}$$

We now substitute the expressions (18)–(21) into Eq. (22), normally order each side with respect to the core, and equate coefficients of $a_r^\dagger a_s$ and $a_r^\dagger a_s^\dagger a_b a_a$ on each side, obtaining

$$(\epsilon_a+\delta E-\epsilon_r)\rho_{ra} = \sum_{b,s}\tilde{g}_{rbas}\rho_{sb}+\sum_{b,s,t}g_{rbst}\tilde{\rho}_{stab}-\sum_{b,c,s}g_{bcas}\tilde{\rho}_{rsbc}\ , \tag{23a}$$

$$\begin{aligned}(\epsilon_a+\epsilon_b+\delta E-\epsilon_r-\epsilon_s)\rho_{rsab} &= g_{rsab}+\sum_{c,d}g_{cdab}\rho_{rscd}+\sum_{t,u}g_{rstu}\rho_{tuab}\\ &\quad+\left[\left(\sum_t g_{rstb}\rho_{ta}-\sum_c g_{csab}\rho_{rc}+\sum_{c,t}\tilde{g}_{cstb}\tilde{\rho}_{rtac}\right)+(a\leftrightarrow b,\ r\leftrightarrow s)\right]\ .\end{aligned} \tag{23b}$$

The final term in the equation indicates that the term in large parentheses is to be repeated with the specified interchange of indices. As before, we have used the tilde notation to denote the inclusion of exchange

$$\tilde{\rho}_{abcd} \equiv \rho_{abcd}-\rho_{abdc}\ . \tag{24}$$

Equations (23) are not unique, because the equation of coefficients of $a_r^\dagger a_s^\dagger a_b a_a$ can be made in more than one way. For example, upon substituting (19) into (22), one obtains terms of the form

$$\sum_{r,s,a,b}(\epsilon_a+\epsilon_b+\delta E-\epsilon_r-\epsilon_s)\rho_{rsab}a_r^\dagger a_s^\dagger a_b a_a|0_C\rangle = \left[\cdots+\sum_{r,s,a,b}\sum_{c,t}g_{cstb}\rho_{rtac}a_r^\dagger a_s^\dagger a_b a_a+\cdots\right]|0_C\rangle \tag{25}$$

leading to the identification

$$(\epsilon_a+\epsilon_b+\delta E-\epsilon_r-\epsilon_s)\rho_{rsab} = \cdots+\sum_{c,t}g_{cstb}\rho_{rtac}+\cdots\ . \tag{26}$$

However, one could equally interchange the summation variables r and s on the right-hand side of (25), anticommute $a_r^\dagger$ and $a_s^\dagger$, and then equate coefficients of $a_r^\dagger a_s^\dagger a_b a_a$, obtaining

$$(\epsilon_a+\epsilon_b+\delta E-\epsilon_r-\epsilon_s)\rho_{rsab} = \cdots-\sum_{c,t}g_{crtb}\rho_{stac}+\cdots\ . \tag{27}$$

In general, any linear combination of the two right-hand side terms (26) and (27) with total weight unity is permissible. These different equations will lead to numerically different results for the pair coefficients ρ_{rsab}, but all physical quantities, such as the correlation energy δE, will turn out the same.

As before, we perform sums over magnetic substates analytically, and reduce (23a) and (23b) to a set of equations involving radial coefficients and angular factors; these are given in Appendix A.

The approach described above is essentially the configuration-interaction method, being completely equivalent to a diagonalization of the no-pair Hamiltonian in the subspace of all possible single and double substitutions in the ground-state configuration. This procedure is exact only for two-electron systems, but may be expected to give a good approximation for closed-shell systems with more electrons. As discussed by Lindgren and Morrison,[5] however, the δE terms on the left-hand sides of (32a) and (23b) generate unphysical "unlinked" diagrams, and are in general better omitted for non-helium-like systems. With this slight modification, Eqs. (23a), (23b), and (21c) constitute the basic pair approximation given by Lindgren and Morrison. More generally, the δE terms can be replaced by coupled-cluster terms. For the special case of helium, however, the δE terms should be included because this renders the treatment exact. An alternative exact formulation for helium is a complete coupled-cluster calculation up to pairs.

A treatment analogous to that given here can also be given for the nonrelativistic Schrödinger equation for helium. In this case, the Coulomb potential formalism and the HF potential formalism (23a) and (23b) are both exact and completely equivalent to one another. For the no-pair equation, however, we would not expect an exact identity between the two formalisms, since the positive energy states in each formalism are defined in different potentials. However, at the level of accuracy of the present calculation we do not observe any discrepancy from the use of the two approaches.

We have written a code to solve the relativistic coupled pair equations for a general closed-shell atom, and can regard the present calculation as a first application of this code on the simplest possible case. These equations also constitute the core sector of the equations for a one-valence-electron atom, so this application is relevant also to our ultimate goal of applying the method to cesium and thallium. For helium, we make the trivial adjustment to the general code of including the δE term in the energy factor on the left-hand side.

The basis set chosen for this calculation involved 30 basis functions, and is thus somewhat smaller than that used for the Coulomb calculation: for this reason a larger error is assigned to the final result. Our approach to the partial-wave extrapolation is quite similar to that used for the Coulomb potential, although there are differences. At a given level of calculation, we now include all excited states with orbital angular momentum $l \le L_{\max}$, and allow all possible values of L, l_1, and l_2 (see Appendix A) consistent with the selection rules. For example, for $L_{\max}=1$, we include s, $p_{1/2}$, and $p_{3/2}$ excited states, and the following angular momentum channels for the pair coefficients: $1s^2 \to s^2(L=0)$, $1s^2 \to s^2(L=1)$, and $1s^2 \to p_{1/2}^2(L=0)$, $1s^2 \to p_{1/2}^2(L=1)$, $1s^2 \to p_{3/2}^2(L=1)$, and $1s^2 \to p_{3/2}^2(L=2)$. A converged solution is obtained for each of $L_{\max}=0,1,2,3,\ldots,7$, and the results extrapolated to $L_{\max} \to \infty$ as described for the Coulomb potential. By adopting this procedure, we ensure that all equivalent forms of the equations (23a) and (23b) give identical results for each value of $L_{\max}$. The partial wave contributions are listed in Table V. The total CRAY cpu time for this calculation was about two hours.

TABLE V. Partial-wave contributions to the all-order HF correlation energy (in units of a.u.).

L	δE	$\delta E(L)$
0	$-0.010\,526\,2$	$-0.010\,526\,2(2)$
1	$-0.038\,836\,9$	$-0.028\,310\,7(2)$
2	$-0.041\,086\,8$	$-0.002\,249\,9(3)$
3	$-0.041\,640\,7$	$-0.000\,553\,9(3)$
4	$-0.041\,838\,0$	$-0.000\,197\,3(4)$
5	$-0.041\,924\,9$	$-0.000\,087\,0(5)$
6	$-0.041\,968\,8$	$-0.000\,043\,9(8)$
7	$-0.041\,993\,3$	$-0.000\,024\,5(9)$
∞	$-0.042\,042(2)$	

The resulting value of the ground-state energy, obtained by adding the extrapolated correlation energy result from Table V to the Hartree-Fock energy is

$$E_{\mathrm{HF}} = -2.903\,855(2)\ \text{a.u.} \tag{28}$$

in agreement with the result of the Coulomb-field calculation.

CONCLUSIONS

We have shown in the above that the use of all-order methods allows one, regardless of starting potential, to reproduce the ground-state energy of helium to seven digits. That energy, as explained in the Introduction, is a theoretical one, and various perturbations must be added to it before comparing with experiment. The present method can also be applied to more realistic calculations in which the corrections described previously are included as perturbations.[11] Since the pair functions are saved after convergence, they can be used to evaluate first-order matrix elements of the Breit operator or of the mass-polarization operator. As with the energy calculation, there will be dependence on the maximum angular momentum used in the pair functions, that can again be extrapolated with the techniques used above. However, since fewer digits are required of these small corrections, a relatively small $L_{\max}$ should suffice. It is an open question as to whether the pair functions can be used in the Lamb shift calculation, though we note that part of the Lamb-shift calculation reduces to evaluating matrix elements of delta functions.

A possible extension of this work would be to treat excited states of helium: only a slight modification of the above formalism is required. Therefore in principle the work reported here can be extended to high-accuracy calculations of arbitrary excited states of helium. However, as noted in the Introduction, our main goal is the calculation of properties of heavy atoms. In these much more complex systems, accuracies of even one percent are already quite good. In this paper we have shown that all-order calculations can be carried out with far higher numerical accuracy. The focus of work on heavy atoms, once these methods have been set up and applied to them, must be the development of techniques to evaluate terms in the perturbation expansion missed by the all-order methods. If they are either negligible or enter only in low orders of perturbation theory, then there is a real possibility of carrying out calculations for heavy atoms with accuracies approaching those of the present work.

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APPENDIX: ANGULAR REDUCTION OF HF PAIR EQUATION

As a preliminary, we note that both the pair coefficients ρ and their antisymmetrized counterparts $\tilde{\rho}$ have angular expansions analogous to Eqs. (11) and (14),

$$\rho_{rsab}=\sum_{L=0}^{\infty} S_L(rsab)J_L(rsab)\ , \tag{A1}$$

$$\tilde{\rho}_{rsab}=\sum_{L=0}^{\infty} \tilde{S}_L(rsab)J_L(rsab)\ , \tag{A2}$$

$$\tilde{S}_L(rsab)=S_L(rsab)+[L]\sum_{L'=0}^{\infty} S_{L'}(srab)\begin{Bmatrix} j_s & j_b & L \\ j_r & j_a & L' \end{Bmatrix}\ ,$$

$$[L]\equiv 2L+1\ . \tag{A3}$$

Here $J_L(rsab)$, given by Eq. (12a), contains the dependence on magnetic quantum numbers, and the "radial" coefficients $S_L(rsab)$ are the quantities solved for numerically. We say that a pair coefficient $S_{L'}(rsab)$ corresponds to the channel $ab\rightarrow\kappa_r\kappa_s(L=L')$; for each channel, the pair coefficients form an $n_r\times n_s$ matrix, where n_r is the number of excited states with angular momentum κ_r included in the basis set. For single excitation coefficients, we require

$$\rho_{ra}=S(ra)\delta(j_r,j_a)\delta(m_r,m_a) \tag{A4}$$

where $S(ra)$ is independent of magnetic quantum numbers.

We can now substitute Eqs. (A1), (A2), and (A4) into Eqs. (23a) and (23b) and project out $J_L(rsab)$ using the JLV4 theorem, as described for the Coulomb equation. We find

$$\begin{aligned}(\epsilon_a+\delta E-\epsilon_r)S(ra)=&\sum_{s,b}\sqrt{[j_s]/[j_a]}\,\delta(j_a,j_r)\delta(j_b,j_s)X_0(rbas)S(sb)\\&+\sum_{s,b,l_1}(-1)^{j_b+j_r+l_1}\frac{1}{[j_r]}\delta(j_a,j_r)\delta(j_b,j_s)X_{l_1}(bras)S(sb)\\&+\sum_{b,s,t,l_1,l_2}(-1)^{j_b+j_t+j_s+j_r}\frac{1}{[j_r][l_2]}\delta(j_a,j_r)\delta(l_1,l_2)X_{l_1}(rbst)\tilde{S}_{l_2}(stab)\\&-\sum_{b,c,s,l_1,l_2}(-1)^{j_b+j_c+j_s+j_r}\frac{1}{[j_r][l_1]}\delta(j_a,j_r)\delta(l_1,l_2)X_{l_1}(bcas)\tilde{S}_{l_2}(rsbc)\ ,\end{aligned} \tag{A5}$$

$$\begin{aligned}&(\epsilon_a+\epsilon_b+\delta E-\epsilon_r-\epsilon_s)S_L(rsab)\\&\quad=X_L(rsab)+\sum_{c,d,l_1,l_2}(-1)^{j_a+j_b+j_r+j_s}[L]\begin{Bmatrix} l_2 & L & l_1 \\ j_a & j_c & j_r \end{Bmatrix}\begin{Bmatrix} l_2 & L & l_1 \\ j_b & j_d & j_s \end{Bmatrix}X_{l_1}(cdab)S_{l_2}(rscd)\\&\qquad+\sum_{t,u,l_1,l_2}(-1)^{j_a+j_b+j_r+j_s}[L]\begin{Bmatrix} l_1 & L & l_2 \\ j_a & j_t & j_r \end{Bmatrix}\begin{Bmatrix} l_1 & L & l_2 \\ j_b & j_u & j_s \end{Bmatrix}X_{l_1}(rstu)S_{l_2}(tuab)\\&\qquad+\Bigg[\Bigg[\sum_{t,l_1}\delta(j_a,j_t)\delta(l_1,L)X_{l_1}(rstb)S(ta)-\sum_{c,l_1}\delta(j_c,j_r)\delta(l_1,L)X_{l_1}(csab)S(rc)\\&\qquad\quad-\sum_{c,t,l_1,l_2}(-1)^{j_c+j_t+L}\frac{1}{[L]}\delta(l_1,l_2)\delta(l_1,L)X_{l_1}(cstb)\tilde{S}_{l_2}(rtac)\\&\qquad\quad-\sum_{c,t,l_1,l_2}(-1)^{j_c+j_t+L}\begin{Bmatrix} l_2 & j_s & j_b \\ l_1 & j_c & j_t \end{Bmatrix}\delta(l_2,L)X_{l_1}(sctb)\tilde{S}_{l_2}(rtac)\Bigg]+(r\leftrightarrow s,a\leftrightarrow b)\Bigg]\ .\end{aligned} \tag{A6}$$

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