CALCULATIONS ON THE HELIUM ISOELECTRONIC SEQUENCE USING COULOMB GREEN'S FUNCTION VARIABLES

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Calculations on the ground states of the helium isoelectronic series are carried out using variational wavefunctions of the form $\psi(x,y)$, in which x and y are the combinations $r_1 + r_2 \pm r_{12}$ occurring in the Coulomb Green's function. The results for helium are the most accurate to date using a two-variable wavefunction, accounting for 71.5% of the correlation energy.

The Coulomb Green's function is the solution under specified boundary conditions of the differential equations [1]:

$$(\tfrac{1}{2}k^2 + \tfrac{1}{2}\nabla_i^2 + Z/r_i)G(r_1,r_2,k) = \delta(r_{12}), \quad i = 1,2.$$

(1)

We use atomic units, whereby $\hbar = e = \mu = 1$. The sum of eqs. (1) over the two particle labels gives

$$(k^2 + \tfrac{1}{2}\nabla_1^2 + \tfrac{1}{2}\nabla_2^2 + Z/r_1 + Z/r_2)G(r_1,r_2,k) = 2\delta(r_{12}),$$

(2)

which closely resembles the Schrödinger equation for a helium-like atom. As shown by Hostler [2], the Coulomb Green's function depends on just two variables:

$$x \equiv r_1 + r_2 + r_{12}, \quad y \equiv r_1 + r_2 - r_{12},$$

(3)

rather than three — say r_1, r_2, r_{12} — which would be expected on the basis of rotational invariance alone. This reduction is a consequence of the SO(4) dynamical symmetry of the Coulomb problem. This higher symmetry is also connected with the existence of an additional constant of the motion, the Runge–Lenz vector.

Specifically the retarded Coulomb Green's function $G^+(x,y,k)$, is given by [3]:

$$G^+(x,y,k) = -(\pi i k)^{-1}(x-y)^{-1}(\partial/\partial x - \partial/\partial y)$$
$$\times \Gamma(1 - i\nu)M_{i\nu}^{1/2}(-iky)W_{i\nu}^{1/2}(-ikx),$$
$$\nu \equiv Z/k, \quad \text{Im}\,k > 0,$$

(4)

in which M and W are Whittaker functions as defined by Buchholz [4].

In this note, we shall explore variational wavefunctions of the form $\psi(x,y)$ to approximate ${}^1S$ states of the helium isoelectronic series. Rigorously, of course, three variables such as r_1, r_2, r_{12} are required to span the functional domain for S states. It is of interest, nevertheless, to see how far one can go with just x and y dependence.

The classical work of Hylleraas [5] was based on the independent variables:

$$s \equiv r_1 + r_2, \quad t \equiv r_1 - r_2, \quad u \equiv r_{12}.$$

(5)

Since $x = s + u$ and $y = s - u$, our computations will be equivalent to those of Hylleraas with the variable t absent.

For helium-like systems, the hamiltonian is given by

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - Z/r_1 - Z/r_2 + 1/r_{12}.$$

(6)

For $\psi = \psi(x,y)$, we write the variational integral

$$E = (\psi, H\psi)/(\psi, \psi) = (T + V)/N,$$

(7)

with

$$N = \frac{1}{48} \int_0^\infty \int_0^x (x^2 + 4xy + y^2)(x-y)^2 |\psi(x,y)|^2 \, dx \, dy, \tag{8}$$

$$T = \frac{1}{12} \int_0^\infty \int_0^x [(x^2 + 2xy)(\partial\psi/\partial x)^2$$
$$+ (y^2 + 2xy)(\partial\psi/\partial y)^2](x-y)^2 \, dx \, dy, \tag{9}$$

$$V = -\frac{1}{4}Z \int_0^\infty \int_0^x (x+y)(x-y)^2 |\psi(x,y)|^2 \, dx \, dy$$
$$+ \frac{1}{24} \int_0^\infty \int_0^x (x^2 + 4xy + y^2)(x-y)|\psi(x,y)|^2 \, dx \, dy. \tag{10}$$

Specifically, we consider linear variational functions of the form

$$\psi(x,y) = e^{-\alpha(x+y)} \sum_{m,n} C_{m,n} x^m y^n. \tag{11}$$

The integrals (8)–(10) are then given explicitly by

$$N = \frac{1}{48} \sum_{m,n,k,l} \{[4,0] + 2[3,1] - 6[2,2]$$
$$+ 2[1,3] + [0,4]\}, \tag{12}$$

$$T = \frac{1}{12}\alpha^2 N - \frac{1}{12} \sum_{m,n,k,l} C_{m,n} C_{k,l}$$
$$\times \{2\alpha[m([3,0] - 3[1,2] + 2[0,3])$$
$$+ n(2[3,0] - 3[2,1] + [0,3])]$$
$$- mk([2,0] - 3[0,2] + 2[-1,3])$$
$$- nl(2[3,-1] - 3[2,0] + [0,2])\}, \tag{13}$$

$$V = \frac{1}{48} \sum_{m,n,k,l} C_{m,n} C_{k,l} \{(-12Z + 2)[3,0]$$
$$+ (12Z + 6)[2,1] + (12Z - 6)[1,2]$$
$$+ (-12Z - 2)[0,3]\}. \tag{14}$$

We have introduced the notation

$$[I,J] \equiv (m + k + I, n + l + J), \tag{15}$$

in terms of the elementary integrals

Table 1
Helium calculations with N-term basis

N	α	$-E$
1	0.84375	2.84765625
3	0.905	2.8912315
6	0.935	2.8916945
10	0.99	2.8917460
15	1.03	2.891750194

$$(m,n) \equiv \int_0^\infty \int_0^x e^{-2\alpha(x+y)} x^m y^n \, dx \, dy$$
$$= \sum_{r=0}^n \frac{(-1)^r n!(m-n-r)!}{(n-r)!(2\alpha)^{r+1}(4\alpha)^{m+n-r+1}} + \frac{n!m!}{(2\alpha)^{n+m+2}}. \tag{16}$$

The functional form (11) trivially includes the simple exponential $\exp[-\alpha(x+y)]$, equivalent to the scaled hydrogenic product $\exp[-2\alpha(r_1 + r_2)]$. This is optimized for $\alpha = 27/32$, giving the approximate helium ground-state energy $E = -2.84765625$ hartree. With the inclusion of sets of linear terms containing higher powers of x and y, we obtain the results summarized in table 1. The exponential parameter has been reoptimized for each basis set. The three-term function $(1, x, y)$ gives an optimal energy of -2.8912315 H. The six-term function (adding x^2, xy, y^2) gives -2.8916504 H. The ten-term function (adding x^3,

Table 2
Coefficients for helium fifteen-term function, $\alpha = 1.03$

$C(0,0)$	1.000000000
$C(1,0)$	0.265456196
$C(0,1)$	−0.175206467
$C(2,0)$	0.017240841
$C(1,1)$	0.080962524
$C(0,2)$	−0.041635911
$C(3,0)$	0.002107589
$C(2,1)$	−0.008768843
$C(1,2)$	0.001859248
$C(0,3)$	−0.000208398
$C(4,0)$	0.000080883
$C(3,1)$	0.001069403
$C(2,2)$	0.000208337
$C(1,3)$	−0.000588844
$C(0,4)$	0.000024063

Table 3
Helium isoelectronic sequence ground-state energies using fifteen-term function

Z	α	$-E$	$-E$(SCF) [a]	$-E$(exact) [b]	% corr
1	0.435	0.50975076	0.48793	0.52759152	55.0
2	1.03	2.89175019	2.86168	2.90372433	71.5
3	1.60	7.26902230	7.23641	7.27991339	75.0
4	2.20	13.64514384	13.61130	13.65556622	76.5
5	2.78	22.02081175	21.98623	22.03097156	77.3
6	3.35	32.39625486	32.36119	32.40624658	77.8
7	3.95	44.77157028	44.73616	44.78144513	78.2
8	4.58	59.14680624	59.11114	59.15659510	78.5
9	5.05	75.52198941	75.48613	75.53171234	78.7

[a] Ref. [7]. [b] Ref. [8].

x^2y, xy^2, y^3) gives −2.8917460 H. Finally, with fifteen terms (adding $x^4, x^3y, x^2y^2, xy^3, y^4$), we obtain −2.891750194 H. The coefficients are shown in table 2. It is estimated that with additional terms the procedure would converge to an approximate energy of −2.89175065 H. Given the exact non-relativistic energy of −2.903724375 H [6] and the Hartree−Fock energy of −2.86168 H [7], it is seen that our calculation accounts for ≈71.5% of the correlation energy of helium.

In table 3, we present analogous calculations, using the fifteen-term function, on the $1s^2$ ^1S ground states of the helium isoelectronic sequence from $Z = 1$ to $Z = 9$. The results are compared with the self-consistent-field calculations of Roothaan and Weiss [7] and the essentially exact 13th-order perturbation calculations of Scherr and Knight [8]. As shown in the last column of table 3, the fraction of correlation energy captured by $\psi(x,y)$ increases to over 75% for two-electron atoms beyond helium.

The calculations on helium-like systems described in this note are the most accurate to date based on wavefunctions dependent on just two variables.

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