Self Consistent Field Calculation Using Two Parameter Wave Function for Helium atom and Helium Like ions

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Abstract:

The application of the self consistent field linear combination (SCF-LCAO) of two Slater type orbitals with two parameters wave function is used to obtain the energy of the 1s state. Calculation is carried out self-consistency in many iteration. The results for the final iterations are compared with experimental results.

Key word: atomic properties/structure, quantum chemistry

Theory

Under the orbital approximation the Hartree wave function for the ground state of the Helium atom has the form:[1]

$$\psi(1,2) = \phi(1)\phi(2) \quad (1)$$

where

$\phi(i)$ is the orbital wave function for an electron .

The problem to be considered is the determination of the orbital best which gives the ground state energy.

ϕ_i can be written as a linear combination of a set of one-electron basis function χ_s [2]

$$\phi_i = \sum_{p=1}^{m} C_p \chi_p \qquad (2)$$

are Slater-type atomic orbitals and the C_p are constants to be χ_p Where the basis function to determined, then the SCF-LCAO equations gives the solution.

These equations for Helium are derived as follows:[3]

The Hamiltonian operator in atomic units for two electron atoms is:

$$H = -\tfrac{1}{2}\nabla_1{}^2 - \tfrac{1}{2}\nabla_2{}^2 - \frac{z}{r_1} - \frac{z}{r_2} + \frac{1}{r_{12}}$$

……(3)

According to the variation theorem[1,4]

$$E = \frac{\int \psi^* H \psi d\tau_1 d\tau_2}{\int \psi^* \psi d\tau_1 d\tau_2}$$

$$= \frac{\int \phi(1)^* \phi(2)^* H \phi(1)\phi(2) d\tau_1 d\tau_2}{\int \phi(1)^* \phi(1) d\tau_1 \int \phi(2)^* \phi(2) d\tau_2}$$

$$= 2\frac{\int \phi(1)^* (-\tfrac{1}{2}\nabla_1{}^2 - \tfrac{z}{r_1})\phi(1) d\tau_1}{\int \phi(1)^* \phi(1) d\tau_1} + \frac{\iint \phi(1)^* \phi(2)^* \tfrac{1}{r_{12}} \phi(1)\phi(2) d\tau_1 d\tau_2}{\int \phi(1)^* \phi(1) d\tau_1 \int \phi(2)^* \phi(2) d\tau_2}$$

..(4)

let

$$g = \frac{\int \phi(2)^* \frac{1}{r_{12}} \phi(2) d\tau_2}{\int \phi(2)^* \phi(2) d\tau_2} \quad \dots(5)$$

And

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$$h = -\frac{1}{2}\nabla_1^{\ 2} - \frac{z}{r_1} \quad \text{. ...(6)}$$

Then

$$E = 2\frac{\langle\phi|h|\phi\rangle}{\langle\phi|\phi\rangle} + \frac{\langle\phi|g|\phi\rangle}{\langle\phi|\phi\rangle} \quad \text{...(7)}$$

Substuting eqn.(2) into eqn.(5) and eqn.(7) we obtain:

$$g = \frac{\sum C_r C_s \int \chi_r(2)\frac{1}{r_{12}}\chi_s(2)d\tau_2}{\sum C_r C_s \int \chi_r(2)\chi_s(2)d\tau_2}$$

...(8)

$$E = \frac{2\sum C_p C_q \langle \chi_p | h | \chi_q \rangle}{\sum C_p C_q \langle \chi_p | \chi_q \rangle} + \frac{\sum C_p C_q \langle \chi_p | g | \chi_q \rangle}{\sum C_p C_q \langle \chi_p | \chi_q \rangle}$$

..(9)

where S_{pq} is the overlap integral.

For simplicity the C_p are assumed to be real and the sums are overall possible values of the indices of the C_p.

The matrix which correspond to the matrix element in eqn.(9) are h,S,and g.

Using eqn.(9) we have:

$$g_{pq} = \frac{\sum C_r C_s \langle \chi_p(1)\chi_r(2) | \frac{1}{r_{12}} | \chi_r(2)\chi_q(1) \rangle}{\sum C_r C_s \langle \chi_r | \chi_s \rangle}$$

....(10)

where the integrals in the numerator are over both electrons.

in eqn.(1),we must find the ϕ_i If we use minimum energy to choose the best minimum of E in eqn.(9)by varying the coefficient C_p.

After differentiation and rearrange equations we have[1,3]

$$2E\sum C_q S_{tq} = 4\sum C_q h_{tq} + 4\sum C_q g_{tq} - \frac{2(\sum C_p C_q g_{pq})(\sum C_q S_{tq})}{\sum C_p C_q S_{pq}}$$

This equation can be rearrange to the form [3]

$$\sum C_q (h_{tq} + g_{tq} - \varepsilon S_{tq}) = 0$$

....(11)

Where

$$\varepsilon = \frac{1}{2}\left(E + \frac{\sum C_p C_q g_{pq}}{\sum C_p C_q S_{pq}}\right) \quad \text{...(12)}$$

If we let

$$F_{tq} = h_{tq} + g_{tq}$$

Eqn.(11) becomes

$$\sum C_q (F_{tq} - \varepsilon . S_{tq}) = 0 \quad :$$

t = 1, 2….m

or in matrix form

$$(F - \varepsilon . S)C = 0 \quad \text{.......(13)}$$

Where F is called the Fock matrix [3] and

$$C = \begin{pmatrix} C_1 \\ \\ \\ C_m \end{pmatrix}$$

Equation (13) is the matrix form of Roothaan equations[1] and has a nontrivial solution for C only when:

$$|F - \varepsilon . S| = 0$$

The parameter ε is called the orbital energy and using eqn.(9)and (12) we have:

$$\varepsilon = \frac{\sum C_p C_q h_{pq} + \sum C_p C_q g_{pq}}{\sum C_p C_q S_{pq}}$$

$$= \frac{\langle \phi | h | \phi \rangle + \langle \phi | g | \phi \rangle}{\langle \phi | \phi \rangle} \quad \ldots(14)$$

Application of SCF-LCAO for Helium atom, after calculating the matrix element is shown in the following equations:[1,3]

For simplicity let us `use a normalized orbital containing just two basis functions:

$$\phi = C_1\chi_1 + C_2\chi_2 \quad \ldots.(15)$$

And

$$\langle \phi | \phi \rangle = \sum C_p C_q S_{pq} = 1 \ldots..(16)$$

Where

$$\chi_1 = 1s(\alpha) = (\tfrac{\alpha^3}{\pi})^{\frac{1}{2}} e^{-\alpha r} \quad \ldots(17)$$

$$\chi_2 = 1s(\beta) = (\tfrac{\beta^3}{\pi})^{\frac{1}{2}} e^{-\beta r} \quad \ldots.(18)$$

The parameters α and β may be varied to give the best energy, but the coefficients C_1 and C_2 must be optimized for each set of values of α and β .The integrals in the matrix element are[1,5]

The elements of h and S are

$$h_{11} = \tfrac{1}{2}\alpha^2 - z\alpha$$

$$= T_{11} + V_{11}$$

$$h_{22} = \tfrac{1}{2}\beta^2 - z\beta$$

$$= T_{22} + V_{22}$$

$$h_{12} = [\tfrac{1}{8}(\alpha+\beta)^2(1-\tau^2)^{2.5}] + [-(\alpha+\beta)^2(1-\tau^2)^{1.5}]$$

$$= T_{12} + V_{12}$$

Where T_{11}, T_{22}, T_{12} are the Kinetic energy integrals

And V_{11}, V_{22}, V_{12} are the electron-nucleus potential energy integrals.

$S_{11}=S_{22}=1$

$$S_{12} = (1-\tau^2)^{\frac{3}{2}}$$

where

$$\tau = \frac{\alpha-\beta}{\alpha+\beta}$$

From eqn.(10) the g_{pq} are

$$g_{11} = C_1^{\,2}\langle \chi_1\chi_1 | \chi_1\chi_1 \rangle + 2C_1C_2\langle \chi_1\chi_1 | \chi_1\chi_2 \rangle + C_2^{\,2}\langle \chi_1\chi_1 | \chi_2\chi_2 \rangle$$

$$g_{22} = C_1^{\,2}\langle \chi_1\chi_1 | \chi_2\chi_2 \rangle + 2C_1C_2\langle \chi_1\chi_2 | \chi_2\chi_2 \rangle + C_2^{\,2}\langle \chi_2\chi_2 | \chi_2\chi_2 \rangle$$

$$g_{12} = C_1^{\,2}\langle \chi_1\chi_1 | \chi_1\chi_2 \rangle + 2C_1C_2\langle \chi_1\chi_2 | \chi_1\chi_2 \rangle + C_2^{\,2}\langle \chi_1\chi_2 | \chi_2\chi_2 \rangle$$

$$\ldots..(19)$$

The integral in eqn.(19) are given by the formula:[1]

$$\langle \chi_1\chi_1 | \chi_1\chi_1 \rangle = V_{1111} = \tfrac{5}{8}\alpha$$

$$\langle \chi_2\chi_2 | \chi_2\chi_2 \rangle = V_{2222} = \tfrac{5}{8}\beta$$

$$\langle \chi_1\chi_1 | \chi_2\chi_2 \rangle = V_{1122} = \tfrac{1}{16}(1-\tau^2)(5-\tau^2)(\alpha+\beta)$$

$$\langle \chi_1\chi_2 | \chi_1\chi_2 \rangle = V_{1212} = \tfrac{5}{16}(1-\tau^2)^3(\alpha+\beta)$$

$$\langle \chi_1\chi_1 | \chi_1\chi_2 \rangle = V_{1112} = \tfrac{1}{32}(1-\tau^2)^{\frac{3}{2}}(1-\tau_1^{\,2})(5-\tau_1^{\,2})(3\alpha+\beta)$$

$$\langle \chi_1\chi_2 | \chi_2\chi_2 \rangle = V_{1222} = \tfrac{1}{32}(1-\tau^2)^{\frac{3}{2}}(1-\tau_2^{\,2})(5-\tau_2^{\,2})(\alpha+3\beta)$$

Where

$$\tau_1 = \frac{\alpha-\beta}{3\alpha+\beta}$$

$$\tau_2 = \frac{\alpha-\beta}{\alpha+3\beta}$$

If we define:

$$H_{11} = g_{11} + T_{11} + V_{11}$$

$$H_{12} = g_{12} + T_{12} + V_{12}$$

$$H_{22} = g_{22} + T_{22} + V_{22}$$

$$\varepsilon_i = \frac{C_{i1}^{\,2}H_{11} + 2C_{i1}C_{i2}H_{12} + C_{i2}^{\,2}H_{22}}{C_{i1}^{\,2} + 2C_{i1}C_{i2}S_{12} + C_{i2}^{\,2}}$$

equation (14) becomes:[6]
….(20)

The energy of the atom is the orbital energy of the i^{th} electron plus the kinetic and nuclear potential energy of the j^{th} electron .

$$E_{atom} = \varepsilon(C_{i1}, C_{i2}) + C_{j1}^{2}(T_{11} + V_{11}) + 2C_{j1}C_{j2}(T_{12} + V_{12}) + C_{j2}^{2}(T_{22} + V_{22})$$

….(21)

Given initial values for the coefficients of the j^{th} electron, minimization of the orbital energy simultaneously with respect to the coefficients of the i^{th} electron yields the orbital energy of the i^{th} electron and its coefficients.

These output coefficients become the input coefficients of the next iteration when the orbital energy of the j^{th} electron is calculated. The procedure is repeated until self-consistency is achieved. This occurs when the out put coefficients are equal to the input coefficients.[6]

Results:

The calculations carried out self-consistency are achieved in many iterations and the results are shown in tables (1,2) for Li^{+1} and B^{+3} respectively.

As the value of the orbital energy and the total energy are recorded for successive iterations the convergence to a self-consistent set of values is clearly apparent. For the final iteration the values are shown in table(3) for Helium sequence.

Table (3) shows the orbital energy, the total energy, and the percentage of error for Helium atom and Helium like ions compared with the experimental values. Table (3) also shows the values of C_{i1},C_{i2}, and the orbital exponent for Helium sequence .

Table(1): The iteration to reach the consistency for Li^{+1}

Iteration	C_1	C_2	$E_{orbital}$	E_{atom}
1	0.810343	0.202227	-2.856272	-7.205022
2	0.835334	0.175949	-2.775451	-7.23443
3	0.832059	0.179401	-2.785856	-7.234937
4	0.832479	0.178955	-2.784481	-7.234956
5	0.832422	0.179015	-2.784669	-7.234937
6	0.832429	0.179007	-2.784645	-7.234937
7	0.832428	0.179008	-2.78465	-7.234933
8	0.832428	0.179008	-2.78465	-7.234933
9	0.832428	0.179008	-2.78465	-7.234933

Table (2) The iteration to reach the consistency for B^{+3}

Iteration	C_1	C_2	$E_{orbital}$	E_{atom}
1	0.816956	0.187525	-9.6026099	-21.951359
2	0.831207	0.172996	-9.522779	-21.981313
3	0.830095	0.174130	-9.528935	-21.981408
4	0.830241	0.1739848	-9.528456	-21.981408
5	0.830169	0.174054	-9.528503	-21.981457
6	0.830177	0.174046	-9.528488	-21.981407
7	0.830193	0.174335	-9.528492	-21.981409
8	0.830177	0.1740465	-9.528480	-21.981465
9	0.830219	0.173997	-9.528491	-21.981409

Table (3):The total energy and the orbital energy compared with the experemantal energy for Helium atom and Helium like ions.

	He	Li^{+}	Be^{+2}	B^{+3}	c^{+4}	N^{+5}	o^{+6}
$E_{orbital}$	0.91816	2.7846	5.6557	9.5284	14.4020	20.2761	27.1505
IP(exp.)[7]	0.9035	2.7795	5.6555	9.5315	14.4051	20.2827	27.1617
Error%	1.6	0.18	0.0035	0.032	0.021	0.032	0.041
E_{atom}	2.86167	7.2349	13.6079	21.9814	32.3555	44.7293	59.1036
E_{atom}(exp.)[8]	2.9037	7.2789	13.6538	22.029	32.4050	44.7827	59.1621
Error%	1.447	0.604	0.336	0.218	0.153	0.119	0.0991
α	1.45[9]	2.45	3.45	4.45	5.45	6.45	7.45
β	2.9[9]	3.9	4.9	5.9	6.9	7.9	8.9
C_1	0.84085	0.8324	0.83055	0.83017	0.83038	0.8307	0.8311
C_2	0.18388	0.1790	0.1760	0.17404	0.17257	0.1715	0.1706

Discussion

An examination of the coefficients and orbital energy for any pair of adjacent iterations in tables (1,2) shows that they bracket the Self consistent values more tightly with each successive iteration.

The total energy of the atom is obtained using the variational principle and decreases gradually with each iteration to a minimum.

This is because for each successive iteration the wave function used to calculate the total energy is an improvement over the one used in the previous iteration.

The SCF energy of Helium is -2.86167 hartree which is more precise as compared with the limiting Hartree-Fock energy Which is -2.861679 found with five basis functions [10].

α and β for Helium, Helium like ions are taken to gives minimum energy in this work .

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حساب طاقة الهليوم وايوناته بواسطة المجال المقوم لذاته ولدالة هارتري ذات متغيرين

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الخلاصة:

استخدمت طريقة المجال المقوم لذاته لحساب طاقة ذرة الهليوم والايونات المشابهة لها للحالة الارضية باستخدام دالة هارتري ذات الجمع الخطي وبمتغيرين وقد قورنت النتيجة مع النتائج التي حصل عليها من التجربة.