

Hartree Equation for the ground state of two electron atoms

Our goal is to find the best wave-function (lowest energy) of the form $\varphi(1)\varphi(2)$ for a two-electron atom. As given above the energy of the atom with this wave-function is

$$E(\varphi) = \langle \varphi(1)\varphi(2) | \hat{H} | \varphi(1)\varphi(2) \rangle = 2 \langle \varphi | \hat{f} | \varphi \rangle + \langle \varphi(1)\varphi(2) | \frac{1}{r_{12}} | \varphi(1)\varphi(2) \rangle$$

If we assume that φ is the best we can do then by augmenting it with a function $\delta\varphi$ and calculating the energy $E(\varphi + \delta\varphi)$ we require that δE be zero to first order in $\delta\varphi$

$$\delta E = E(\varphi + \delta\varphi) - E(\varphi) = 0(\delta\varphi)$$

so forming

$$E(\varphi + \delta\varphi) = 2 \langle \varphi + \delta\varphi | \hat{f} | \varphi + \delta\varphi \rangle + \langle (\varphi(1) + \delta\varphi(1))(\varphi(2) + \delta\varphi(2)) | \frac{1}{r_{12}} | (\varphi(1) + \delta\varphi(1))(\varphi(2) + \delta\varphi(2)) \rangle$$

and assuming φ is real, we have (after some algebra)

$$\delta E = 4 \langle \delta\varphi | \hat{f} | \varphi \rangle + 4 \langle \delta\varphi(1)\varphi(2) | \frac{1}{r_{12}} | \varphi(1)\varphi(2) \rangle = 4 \int \delta\varphi(1) \left(\hat{f} + \int \varphi(2) \frac{1}{r_{12}} \varphi(2) dV(2) \right) \varphi(1) dV(1)$$

To insure that the variation in φ maintains normalization we will add the term

$\langle \varphi + \delta\varphi | \varphi + \delta\varphi \rangle - \langle \varphi | \varphi \rangle = 2 \langle \delta\varphi | \varphi \rangle = 2 \int \delta\varphi(1)\varphi(1) dV(1)$ with the Lagrangian multiplier λ and vary φ arbitrarily

$$\delta E + \lambda 2 \langle \delta\varphi | \varphi \rangle = 0$$

or

$$\delta E + 2\lambda \int \delta\varphi(1)\varphi(1) dV(1) = 4 \int \delta\varphi(1) \left(\hat{f} + \int \varphi(2) \frac{1}{r_{12}} \varphi(2) dV(2) + \lambda / 2 \right) \varphi(1) dV(1) = 0$$

for this to be true for arbitrary variations we must have

$$\left(\hat{f} + \int \varphi(2) \frac{1}{r_{12}} \varphi(2) dV(2) + \lambda / 2 \right) \varphi(1) = 0$$

Defining the Coulomb operator

$\hat{J} = \int \varphi(2) \frac{1}{r_{12}} \varphi(2) dV(2)$, the Fock operator, $\hat{F} = \hat{f} + \hat{J}$ and $-\frac{\lambda}{2} = \varepsilon$ we have the pseudo eigenvalue equation

$$\hat{F}\varphi = \varepsilon\varphi$$

This is a pseudo eigenvalue problem because the Fock operator depends on the solution via the Coulomb operator \hat{J} . Problems of this type are solved in a self-consistent-way by estimating (guessing) the solution, say φ_0 , forming the Fock operator with this estimate and finding the eigenfunction, say φ_1 and eigenvalue of this approximate Fock operator. One can then compare the energies $E(\varphi_0)$ & $E(\varphi_1)$ and if they are different (to a pre-determined amount) form the Fock operator with the current eigenfunction φ_1 , solve the eigenvalue problem to get a new function φ_2 , compare the energies $E(\varphi_1)$ & $E(\varphi_2)$ and if they are different repeat the procedure until the energy of the input equals the energy of the output. When we do this we find $E = -2.8617$ and $-\varepsilon = 0.9179au$. Note while this is the lowest energy one can have for a simple product function it is only slightly more negative than that found above (-0.014au) for the product of two 1s functions with optimized exponents.

To see what the eigenvalue ε means we write the energy as

$$E(\varphi) = \langle \varphi | 2\hat{f} + \hat{J} | \varphi \rangle = \langle \varphi | \hat{f} + \hat{F} | \varphi \rangle = \langle \varphi | \hat{f} | \varphi \rangle + \varepsilon$$

If we remove an electron and assume that the orbital φ doesn't change, the energy of the resulting ion is $\langle \varphi | \hat{f} | \varphi \rangle$ and so $-\varepsilon (= 0.9179au)$ is, approximately, the first ionization energy, (experimental $0.9037au$). Part of the error in the predicted ionization energy comes from the approximation that φ doesn't change when we remove an electron and clearly it does because its been optimized for the two electron system. By the variation principle the energy of the ion is lower than $\langle \varphi | \hat{f} | \varphi \rangle$ say $\langle \varphi | \hat{f} | \varphi \rangle - \delta$ where δ is positive. With this correction the ionization energy is $-(\varepsilon + \delta)$, higher than experiment, suggesting that $\delta \sim 0.015$. This is an example of Koopmann's theorem that we will return to latter.

How to solve $\hat{F}\varphi = \varepsilon\varphi$?

Lets go into more detail into how one solves the Fock equation for these systems. Usually one approximates the orbital φ as a linear combination of orbitals of S symmetry

$$\varphi = \sum_{i=1}^N c_i \chi_i \text{ where } \chi_i = \sqrt{\frac{\alpha_i^3}{\pi}} e^{-\alpha_i r} \text{ and where one determines } c_i \text{ \& } \alpha_i \text{ so that the}$$

energy $E(\varphi)$ is a minimum. The χ_i (often called basis functions) in this instance are simply 1s orbitals with effective nuclear charges α_i to be determined. Lets see how

$$\text{this works for } N=2 \text{ when } \varphi = c_a \chi_a + c_b \chi_b \text{ and } \chi_a = \sqrt{\frac{a^3}{\pi}} e^{-ar} \text{ \& } \chi_b = \sqrt{\frac{b^3}{\pi}} e^{-br} .$$

There are 4 unknowns; the two exponents a & b and the two coefficients, c_a & c_b . We begin by guessing the two exponents, and both coefficients, and calculating the energy of He for the resulting orbital. This is the zero iteration energy. Keeping the exponents we then begin the iteration process to determine the coefficients appropriate for these exponents. We calculate the energy of this function and compare it with the zero iteration and if the difference is greater than 10^{-6} , we repeat the process until the difference between the current the previous energy is less than 10^{-6} .

We show in the appendix that this results in $a = 1.45$ & $b = 2.89$ and with these exponents we have $c_a = 0.83955$, $c_b = 0.18503$, $\varepsilon = -0.917981 au$ & $E = -2.861672 au$. Note that while we have only used two functions to expand the orbital φ we have calculated the Hartree energy accurately to 6 decimal places.

We collect in the following table Hartree results for the ground state of the two electron atoms through N^{+5} using two basis functions and compare these to the exact Hartree results. It's interesting that the total energy for a given atom is essentially the same in both sets of calculations while the orbital looks significantly different. For example for N^{+5} our orbital is defined by the parameters $a = 6.41, b = 10.69, c_a = 0.93573$ & $c_b = 0.07034$ while Huzinaga and Arnau have $a = 6.00, b = 8.53, c_a = 0.73309$ & $c_b = 0.27600$. However the overlap between these two functions is 0.99976 suggesting that they are essentially the same orbital and it's the non-linear nature of the optimization that couples the exponents and coefficients.

atom	a	b	c_A	c_B	$\varepsilon(au)$	$E(au)$
He	1.45 (1.45)*	2.89 (2.92)*	0.83955 (0.84340)	0.18508 (0.18153)	-0.917981 (-0.918488)	-2.861672 (-2.861666) -2.861680**
Li ⁺	2.48 (2.48)*	4.86 (4.69)*	0.91353 (0.905631)	0.10046 (0.10786)	-2.791509 (-2.789893)	-7.236370 (-7.236307) -7.236415**
Be ⁺²	3.45	6.29	0.91725	0.09338	-5.666991	-13.611297

	(3.35)*	(5.54)*	(0.84912)	(0.16322)	(-5.668692)	(-13.611092) -13.611299**
B^{+3}	4.45 (4.25)*	7.95 (6.55)*	0.93254 (0.81376)	0.07569 (0.19696)	-9.541575 (-9.544651)	-21.986230 (-21.985603) -21.986234**
C^{+4}	5.43 (5.11)*	9.38 (7.48)*	0.93538 (0.76110)	0.07162 (0.24883)	-14.417079 (-14.420657)	-32.361187 (-32.359744) -32.361193**
N^{+5}	6.41 (6.00)*	10.69 (8.53)*	0.93573 (0.73309)	0.07034 (0.27600)	-20.292174 (-20.29615)	-44.736139 (-44.733953) -44.736164**

The first set of numbers for each atom are those obtained by optimizing the orbital exponents in a two STO expansion of the Hartree-Fock wavefunction .

*exponents taken from S. Huzinaga and C. Arnau, *J. Chem. Phys.* 53, 451-452 (1970) for the neutral atoms..** Exact Hartree Energy from E. R. Davidson, et. al, *Physical Review A.* 44,7071, 1991

Appendix . How to solve $\hat{F}\varphi = \varepsilon\varphi$?

Lets go into more detail into how one solves the Fock equation for these systems. Usually one approximates the orbital φ as a linear combination of orbitals of S symmetry

$\varphi = \sum_{i=1}^N c_i \chi_i$ where $\chi_i = \sqrt{\frac{\alpha_i^3}{\pi}} e^{-\alpha_i r}$ and where one determines c_i & α_i so that the

energy $E(\varphi)$ is a minimum. The χ_i (often called basis functions) in this instance are simply 1s orbitals with effective nuclear charges α_i to be determined. Lets see how

this works for $N=2$ when $\varphi = c_a \chi_a + c_b \chi_b$ and $\chi_a = \sqrt{\frac{a^3}{\pi}} e^{-ar}$ & $\chi_b = \sqrt{\frac{b^3}{\pi}} e^{-br}$. There

are 4 unknowns; the two exponents a & b and the two coefficients, c_a & c_b . We begin by guessing the two exponents, and both coefficients, and calculating the energy of He for the resulting orbital. This is the zero iteration energy. Keeping the exponents we then begin the iteration process to determine the coefficients appropriate for these exponents. We calculate the energy of this function and compare it with the zero iteration and if the difference is greater than 10^{-6} , we repeat the process until the difference between the current the previous energy is less than 10^{-6} .

Now lets begin by guessing the exponents. We have seen that the optimal exponent when the trial function is a single exponential is $27/16$ or 1.6875 so a reasonable initial choice would be one larger and one smaller, say 1.4 and 2.0 . It turns out that we only need to estimate one coefficient because they are constrained by normalization of φ .

$$\langle \varphi | \varphi \rangle = 1 = \langle c_a \chi_a + c_b \chi_b | c_a \chi_a + c_b \chi_b \rangle = c_a^2 + c_b^2 + 2c_a c_b \Delta$$

Note that Δ is determined by the exponents

$$\Delta_{ab} = 8 \frac{(ab)^{3/2}}{(a+b)^3} = 0.95365279$$

if we choose $c_a = 0.8$ we must have $c_b = 0.207671$.

The energy is given by

$$E = 2 \langle \varphi | \hat{f} | \varphi \rangle + \langle \varphi(1)\varphi(2) | \frac{1}{r_{12}} | \varphi(1)\varphi(2) \rangle = E_1 + E_2$$

where the one electron energy

$$E_1 = 2 \langle \varphi | \hat{f} | \varphi \rangle = 2.0 * c_a^2 f_{aa} + 4.0 * c_a c_b f_{ab} + 2.0 * c_b^2 f_{bb}$$

The one-electron matrix elements are special cases of the general formula

$$f_{\mu\nu} = \left(\frac{\mu\nu - Z(\mu + \nu)}{2} \right) \Delta_{\mu\nu}$$

The two electron energy is

$$E_2 = c_a^4 \langle aa | aa \rangle + 4.0 * c_a^3 c_b \langle aa | ab \rangle + 4.0 * c_a^2 c_b^2 \langle aa | bb \rangle + 2.0 * c_a^2 c_b^2 \langle ab | ab \rangle + 4.0 * c_a c_b^3 \langle ab | bb \rangle + c_b^4 \langle bb | bb \rangle$$

where in a notation we will use frequently

$$\langle ik | jl \rangle = \langle \chi_i(1)\chi_k(2) | \frac{1}{r_{12}} | \chi_j(1)\chi_l(2) \rangle$$

We evaluated an integral similar to this earlier so in a similar way

using $\frac{1}{r_{12}} = \sum_{\ell=0}^{\infty} \frac{r_{<}^{\ell}}{r_{>}^{\ell+1}} P_{\ell}(\theta_{12})$ we have

$$\langle \chi_i(1)\chi_k(2) | \frac{1}{r_{12}} | \chi_j(1)\chi_l(2) \rangle = 16 (\alpha_i \alpha_j \alpha_k \alpha_l)^{3/2} \int_0^{\infty} e^{-(\alpha_i + \alpha_j)r_1} r_1^2 dr_1 \left(\frac{1}{r_1} \int_0^{r_1} e^{-(\alpha_k + \alpha_l)r_2} r_2^2 dr_2 + \int_{r_1}^{\infty} e^{-(\alpha_k + \alpha_l)r_2} r_2 dr_2 \right)$$

and so

$$\langle ik|jl\rangle = 32(\alpha_i\alpha_j\alpha_k\alpha_l)^{3/2} \left(\frac{g^2 + 3gh + h^2}{g^2h^2(g+h)^3} \right) \text{ where } g = \alpha_i + \alpha_j \text{ \& } h = \alpha_k + \alpha_l$$

The required two electron integrals are special cases of this general formula. For example

$$\langle aa|aa\rangle = \frac{5}{8}a$$

$$\langle ab|ab\rangle = \frac{ab(a^2 + 3ab + b^2)}{(a+b)^3}$$

and

$$\langle aa|ab\rangle = 8(a^3b)^{3/2} \left(\frac{4a^2 + 6a(a+b) + (a+b)^2}{a^2(a+b)^2(3a+b)^3} \right)$$

etc. Note by symmetry

$$\langle ab|ab\rangle = \langle ba|ba\rangle$$

and

$$\langle aa|ab\rangle = \langle aa|ba\rangle = \langle ab|aa\rangle = \langle ba|aa\rangle$$

Using $a = 1.4$ & $b = 2.0$ we can evaluate the various matrix elements

$$f_{aa} = -1.82, f_{ab} = -1.9073056, f_{bb} = -2.0$$

$$\langle aa|aa\rangle = 0.875, \langle aa|ab\rangle = 0.9134483, \langle aa|bb\rangle = 0.96629449$$

$$\langle ab|ab\rangle = 1.02300023, \langle ab|bb\rangle = 1.09397171, \langle bb|bb\rangle = 1.25$$

and so

$$E_1 = -1.82c_a^2 - 3.8146112c_a c_b - 2.0c_b^2$$

and

$$E_2 = 0.875c_a^4 + 3.65393932c_a^3c_b + 3.86517796c_a^2c_b^2 + 2.04600046c_a^2c_b^2 + 4.37588684c_a c_b^3 + 1.25c_b^4$$

Using the initial estimate $c_a = 0.8$ & $c_b = 0.207671$ we have for the zero iteration energy

$$E^0 = E_1^0 + E_2^0 = -3.769603562 + 0.952783327 = -2.81682au$$

We now want to update the coefficients.

First multiply the Fock equation by χ_a and integrate, first for the left hand side

$$\langle \chi_a | \hat{F} | \varphi \rangle = \langle \chi_a | \hat{F} | c_a \chi_a + c_b \chi_b \rangle = c_a \langle \chi_a | \hat{F} | \chi_a \rangle + c_b \langle \chi_a | \hat{F} | \chi_b \rangle = c_a F_{aa} + c_b F_{ab}$$

and now for the right

$$\varepsilon (c_a + c_b \langle \chi_a | \chi_b \rangle) = \varepsilon (c_a + c_b \Delta)$$

and so

$$c_a F_{aa} + c_b F_{ab} = \varepsilon (c_a + c_b \Delta)$$

where $\Delta = \langle \chi_a | \chi_b \rangle$ is the overlap integral. Multiplying the Fock equation by χ_b and integrating results in a second equation

$$c_a F_{ba} + c_b F_{bb} = \varepsilon (c_a \Delta + c_b)$$

and eliminating ε results in

$$\frac{c_a F_{aa} + c_b F_{ab}}{c_a + c_b \Delta} = \frac{c_a F_{ba} + c_b F_{bb}}{c_a \Delta + c_b}$$

and after dividing through by c_b and using $R = \frac{c_b}{c_a}$ we have

$$\frac{F_{aa} + RF_{ab}}{1 + R\Delta} = \frac{F_{ba} + RF_{bb}}{\Delta + R}$$

or

$$AR^2 + BR + C = 0$$

Where $A = F_{ab} - \Delta F_{bb}$, $B = F_{aa} - F_{bb}$ & $C = \Delta F_{aa} - \Delta F_{ab}$

And so

$$R = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$$

We will use the initial estimate to evaluate A, B & C

Let's construct the Fock matrix elements.

$$F_{aa} = \langle \chi_a | \hat{f} + \hat{J} | \chi_a \rangle = f_{aa} + J_{aa}$$

The one-electron terms don't change with iterations so for the Coulomb term lets look first at the operator

$$\hat{J} = \int \varphi(2) \frac{1}{r_{12}} \varphi(2) dV(2) = \int (c_a \chi_a(2) + c_b \chi_b(2)) \frac{1}{r_{12}} (c_a \chi_a(2) + c_b \chi_b(2)) dV(2)$$

and so

$$\hat{J} = c_a^2 \int \chi_a^2(2) \frac{1}{r_{12}} dV(2) + c_b^2 \int \chi_b^2(2) \frac{1}{r_{12}} dV(2) + 2c_a c_b \int \chi_a(2) \chi_b(2) \frac{1}{r_{12}} dV(2)$$

and then the matrix element

$$J_{aa} = \langle \chi_a | \hat{J} | \chi_a \rangle = c_a^2 \langle aa | aa \rangle + c_b^2 \langle ab | ab \rangle + 2c_a c_b \langle aa | ab \rangle$$

$$F_{aa} = \langle \chi_a | f + \hat{J} | \chi_a \rangle = -1.82 + 0.875c_a^2 + 1.023c_b^2 + 1.82696966c_a c_b$$

and in a similar fashion we have

$$F_{bb} = \langle \chi_b | f + \hat{J} | \chi_b \rangle = -2.00 + 1.023c_a^2 + 1.25c_b^2 + 2.1879434c_a c_b$$

$$F_{ab} = F_{ba} = \langle \chi_a | f + \hat{J} | \chi_b \rangle = -1.90730558 + 0.913484835c_a^2 + 1.09397171c_b^2 + 1.93258898c_a c_b$$

Using the initial estimate for c_a & c_b we have

$$F_{aa} = -0.912353926, F_{bb} = -0.927872879, F_{ab} = -0.954421159$$

and so $A = 0.0435229$, $B = 0.01551895$, $C = -0.0695526$ and taking the positive sign

$R = 0.82070543$ and from the normalization requirement we have an updated

$$c_a = (1 + 2R\Delta + R^2)^{-1/2} = 0.45602534 \text{ and from } c_b = Rc_a \text{ we have } c_b = 0.55565045$$

Using the updated coefficients we evaluate the one and two electron contributions to the energy through iteration 1.

$$E^1 = E_1^1 + E_2^1 = -3.925134724 + 1.0714213 = -2.8537134au$$

and in addition, we compute the eigenvalue using

$$\varepsilon = \frac{c_a F_{aa} + c_b F_{ab}}{c_a + c_b \Delta} = -0.9598945au$$

Since $E^0 = -2.81682au$, and $E^0 - E^1 = 0.03689au$, considerably greater than 10^{-6} , we initiate iteration 2. Using the most recent coefficients we evaluate the Fock matrix elements, calculate $A, B, \& C$, compute an updated R and then c_a & c_b . Using these coefficients we calculate E^2 , compare it to E^1 . The procedure converges very quickly as seen from the data in the table below.

iteration	c_a	c_b	$-F_{aa}$	$-F_{ab}$	$-F_{bb}$	$-\varepsilon$	$-E$
0	0.8	0.2076	0.9124	0.9544	0.9279		2.816820
1	0.4560	0.5557	0.8592	0.8899	0.8469	0.95989	2.853713
2	0.5458	0.4660	0.8727	0.9062	0.8675	0.89240	2.855579
3	0.5226	0.4892	0.8692	0.9020	0.8621	0.90928	2.855705
4	0.5286	0.4832	0.8701	0.9031	0.8635	0.90486	2.855713
5	0.5270	0.4847	0.8698	0.9028	0.8632	0.90601	2.855714
6	0.5274	0.4843				0.90571	2.855714

Given a & b we know how to solve for c_a & c_b so we now focus on finding the optimal exponents. A little exploration will reveal that the optimal a lies between 0.4 and 0.5 while the optimal b is between 2.7 and 3.0. We calculate the energy for a grid of a & b and collect the results in table xxx. Note that the energy is not very sensitive to the exponents.

		b		
a	2.7	2.8	2.9	3.0

1.3	-2.858686	-2.857216	-2.855461	-2.853459
1.4	-2.861554	-2.861371	-2.860994	-2.860441
1.5	-2.860325	-2.860786	-2.861132	-2.861370
1.6			-2.856847	-2.857318

From which we can determine $a = 1.45$ & $b = 2.89$ and with these exponents we calculate $c_a = 0.83955$, $c_b = 0.18503$, $\epsilon = -0.917981au$ & $E = -2.861672au$. Note that while we have only used two functions to expand the orbital ϕ we have calculated the Hartree energy accurately to 6 decimal places.