match no. 24 pp. 73-84 1989

CONCERNING THE HARTREE-FOCK ENERGIES OF N-ELECTRON ATOMIC SYSTEMS WITH ATOMIC NUMBER Z > Zo(N)

Marek Fraczak

The Fundamental Chemistry Institute, Technical University of Szczecin: Al. Piastow 42, 71-065 Szczecin, Poland

(Received: July 1988)

ABSTRACT. A second order recurrence relation for the Hartree-Fock energies of N-electron atomic systems is presented. The resulting energy formula is shown to be asymptotically exact. Besides, this energy expression is proved to be compatible with the 1/Z perturbation expansion.

1. INTRODUCTION

Practical methods for determining approximate solutions to the Schrodinger equation, $H\psi = E\psi$, are often based on the variational principle $\delta\langle H\rangle = 0$, where $\langle H\rangle = \langle\phi|H|\phi\rangle/\langle\phi|\phi\rangle$ and ϕ is the trial wave function. The classical example is the one-parameter function $\phi(1,2) = (\zeta^3/\pi)\exp[-\zeta(r_1 + r_2)]$ which leads to the well known formula for the ground state total energy of two-electron atomic systems [1]:

$$E(Z;2) = -(Z - 5/16)^2, \text{ a.u.} \qquad (1)$$

When compared with the Hartree-Fock value of E (-2.861697) for helium, where Z = 2, that calculated via EQ.1 (-2.847656) is seen to be about 0.5% (5000 ppm) higher. In order to increase the accuracy of the variational method, one has to take a more sophisticated test function with more adjustable parameters, so that, by minimizing the energy integral $\langle H\rangle$, a closer approximation to the correct energy could be made [2].

The unquestionable record-breaking number of parameters is that introduced by Pekeris [3] who expanded $\phi(1,2)$ to over 10^3 terms (Kinoshita [4] chose the 80-term function). In view of this, the one-parameter EQUATION (1) might seem to be unworthy to notice. It is therefore surprising enough that this over-simplified energy formula leads to the exact expression for the average electron-nuclear attraction energy, V_{ne}, at least for 30-term long series of systems with $Z > 6$. The adjective "exact" is used here for the statement that the relative errors of the function

$$V_{ne} = Z(dE/dZ) = -(2Z - 5/8)Z, \qquad (2)$$

which do not exceed 1.7 ppm (TABLE 1), are considerably (about 10 times) smaller than those of the RHF-SCF computations themselves [5], the latter being determined from the virial theorem test. Accordingly, the tiny differences between the values of V_{ne} calculated from EQUATION (2) and the actual Hartree-Fock data can be considered insignificant.

In conclusion, we note that, as it follows from EQ.(2), for $N = 2$ and $Z > 6$, the second derivative of the HF-energy is constant and equal to -2, that is to say, $d^2E(Z;2)/dZ^2 = -2$. It might be argued that this conclusion could have been readily anticipated from the fact that electron-nuclear interactions predominate over electron-electron interactions for highly ionized atoms; the Z^2 dependence of the hydrogenic orbital energies leads directly to the constancy of the second derivative. However, it is not exactly the case. For example, if $Z = 10$, the electron-electron repulsion energy $V_{ee}(10;2)$ is equal to 6.02753 a.u., which is more than 6% of the total Hartree-Fock energy (-93.86111 a.u.) and, therefore, can hardly be ignored.

In view of this, it seems interesting to find out whether the similar sort of relation holds true for the higher-N isoelectronic series. In the following SECTION, we shall try to solve this problem for $N = 3, 4, \ldots, 10$.

TABLE 1. Comparison of the electron-nuclear attraction energies predicted from EQ.(2) with the actual RHF-values

Z	$-V_{ne}$, EQ.(2)	$-V_{ne}$, RHF	RE of EQ.(2)	RE of VTT
7	93.62500	93.62486	1.5	-4.4
8	123.00000	122.99992	0.6	-7.0
9	156.37500	156.37473	1.7	13.7
10	193.75000	193.74975	1.3	12.7
11	235.12500	235.12476	1.0	10.1
12	280.50000	280.49979	0.75	8.0
13	329.87500	329.87483	0.51	6.4
14	383.25000	383.24982	0.47	6.2
15	440.62500	440.62483	0.39	4.8
16	502.00000	501.99987	0.26	3.8
17	567.37500	567.37486	0.25	3.4
18	636.75000	636.74988	0.19	3.0
19	710.12500	710.12490	0.14	2.5
20	787.50000	787.49990	0.13	2.2
21	868.87500	868.87489	0.13	1.9
22	954.25000	954.24991	0.094	1.4
23	1043.62500	1043.62493	0.067	1.3
24	1137.00000	1136.99995	0.044	0.90
25	1234.37500	1234.37492	0.065	0.65
26	1335.75000	1335.74994	0.045	0.55
27	1441.12500	1441.12494	0.041	0.50
28	1550.50000	1550.49996	0.026	0.10
29	1663.87500	1663.87496	0.024	-0.05
30	1781.25000	1781.24998	0.011	-0.10
31	1902.62500	1902.62498	0.011	-0.20
32	2028.0000	2027.9999	0.049	-0.35
33	2157.3750	2157.3749	0.046	-0.30
34	2290.7500	2290.7499	0.044	-0.50
35	2428.1250	2428.1249	0.041	-0.50
36	2569.5000	2569.4999	0.039	-0.55
		mean	0.332	3.27

RHF - Roothaan-Hartree-Fock values in atomic units (REF.5)

RE - Relative Error, parts per milion

VTT - Virial Theorem Test. This theorem predicts a value of -2 for the ratio of the potential and kinetic energies; RE(VTT) = $[(VTT + 2)/2]10^6$. Numerical values of VTT are taken from REF.5.

2. RECURRENCE RELATION FOR THE HARTREE-FOCK ENERGIES

The finite difference counterpart of the second derivative, d^2E/dZ^2, is defined as

$$D^2(Z;N) \equiv E(Z+2;N) - 2E(Z+1;N) + E(Z;N). \quad (3)$$

Taking the Hartree-Fock energies [6] as the basis for computations, let us examine the Z-dependence of this quantity for the different numbers N of electrons. In TABLE 2, the values of D^2 are displayed with the exactitude of four digits:

TABLE 2. Numerical values of $-D^2(Z;N)$, EQ.(3)

Z	N = 3	N = 4	N = 5	N = 6	N = 7	N = 8	N = 10
3	2.254						
4	2.251	2.506					
5	2.251	2.503	2.760				
6	**2.250**	2.502	2.755	3.013			
7	2.250	2.501	2.753	3.007	3.265		
8	2.250	**2.500**	2.752	3.004	3.258	3.518	
9	2.250	2.500	2.751	3.003	3.256	3.511	
10	2.250	2.500	2.751	3.002	3.254	3.508	4.024
11	2.250	2.500	2.751	3.001	3.253	3.505	4.016
12	2.250	2.500	2.751	3.001	3.252	3.504	4.011
13	2.250	2.500	**2.750**	3.001	3.252	3.503	4.008
14	2.250	2.500	2.750	3.001	3.251	3.502	4.006
15	2.250	2.500	2.750	3.001	3.251	3.502	4.005
16	2.250	2.500	2.750	**3.000**	3.251	3.502	4.003
17	2.250	2.500	2.750	3.000	3.251	3.501	4.003
18	2.250	2.500	2.750	3.000	3.251	3.501	4.003
19	2.250	2.500	2.750	3.000	**3.250**	3.501	4.002
20	2.250	2.500	2.750	3.000	3.250	3.501	4.002
21	2.250	2.500	2.750	3.000	3.250	3.501	4.002
22	2.250	2.500	2.750	3.000	3.250	3.501	4.001
23	2.250	2.500	2.750	3.000	3.250	**3.500**	4.001
24	2.250	2.500	2.750	3.000	3.250	3.500	4.002
25	2.250	2.500	2.750	3.000	3.250	3.501	4.000
26	2.250	2.500	2.750	3.000	3.250	3.501	4.001
27	2.250	2.500	2.750	2.999	3.251	3.499	4.001
28	2.250	2.499	2.750	3.002	3.249	3.500	4.001
29	2.250	2.501	2.750	2.998	3.251	3.500	**4.000**
30	2.250	2.500	2.751	3.002	3.250	3.500	4.000

Two features of the results reported in TABLE 2 are of a special interest. First, as is seen, for sufficiently large Z, $D^2(Z;N)$ comes up to its limit $Y = Y(N)$, where

$$Y(N) = -(6 + N)/4 \qquad (4)$$

and N = (2),3,4, ... ,(9),10 (for consideration of space, the cases of N = 2 and N = 9 are not included in TAB.2). Secondly, the convergence $D^2(Z;N) \dashrightarrow Y(N)$ appears to be slower for the higher numbers N of electrons. In other words, for $Z > Zo(N)$, $|D^2(Z;N) - Y(N)| < \varepsilon$, where ε is an optionally small positive number and Zo(N) is an increasing function of N.

It should be remarked here that, according to TABLE 2, the above statement has been proved to be valid for $\varepsilon \geq 0.001$. This restriction is related to the fact that the differentiation of a function specified only by a table of values is a notoriously unsatisfactory process, particularly if higher derivatives than the first are required [7].

Our purpose is now to express total energies of atomic systems by using the relation $D^2(Z;N) = Y(N)$ which is expected to be sufficiently accurate for $Z > Zo(N)$, where Zo can be taken from TAB.(2) according to the desired exactitude of the resulting formula. By comparing the right hand sides of EQUATIONS (3) and (4), we get

$$E(Z+2;N) - 2E(Z+1;N) + E(Z;N) = -(6+N)/4. \qquad (5)$$

It is iluminating to write this equation in an alternative way:

$$E(Z+2) - E(Z+1) = E(Z+1) - E(Z) + Y, \qquad (6)$$

where N is understood to be fixed. As it is now clearly seen, E(Z) can be determined by the recurrence procedure evidently related to an arithmetical sequence. Indeed, starting from E(Zo), we have

$$E(Zo+1) = E(Zo) + Y + P \qquad (7)$$
$$E(Zo+2) = E(Zo+1) + 2Y + P = E(Zo) + (1+2)Y + 2P$$
$$E(Zo+3) = E(Zo+2) + 3Y + P = E(Zo) + (1+2+3)Y + 3P$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$E(Zo+k) = E(Zo+k-1) + kY + P = E(Zo) + (1+2+3+\ldots+k)Y + kP,$$

where $P = P(Zo;N)$ is an "integration" constant which, being independent of Z for $Z > Zo$, does depend on Zo:

$$P = E(Zo+1) - E(Zo) - Y. \qquad (8)$$

Now, since $k = Z-Zo$ and $1+2+3+\ldots+k = k(k+1)/2$, we get the following energy expression

$$E(Z) = E(Zo) + (P + Y/2)(Z-Zo) + (Y/2)(Z-Zo)^2 \qquad (9)$$

or, alternatively

$$E(Z) = E(Zo) + [E(Zo+1) - E(Zo) - Y/2](Z-Zo) + (Y/2)(Z-Zo)^2 \qquad (10)$$

where, according to EQ.(4), $Y/2 = -(6+N)/8$.

As there are no parameters to be fitted, EQUATION 10 can be formally considered as a parameter-free energy formula provided the total energies, E(Zo) and E(Zo+1), of the two adjacent members in a given isoelectronic series are known. Let us then get an idea of the accuracy of EQUATION 10. Mainly for consideration of space, let $Zo = 25$ be the common starting point for each $N = 2,3,\ldots,10$. In TABLE 3, the Hartree-Fock energies are compared with those obtained from EQ.(10). It is seen that our energy expression is extremely accurate as its error does not exceed several parts per million. For the lower-N isoelectronic series, this EQUATION could even be said to be an exact energy formula. The increasing absolute error for the higher-N series finds its direct explanation in the slower convergence of $D^2(Z;N)$ to the limit Y(N).

TABLE 3. Comparison of the energies predicted from EQ.(10) with the actual Hartree-Fock data*

Z	-E(Z).EQ.10	-E(Z).HF	-E(Z).EQ.10	-E(Z).HF
	(N = 2)		(N = 3)	
27	712.2361	712.2361	792.8655	792.8655
28	766.6111	766.6111	853.7176	853.7177
29	822.9861	822.9861	916.8197	916.8198
30	881.3611	881.3611	982.1718	982.1720
31	941.7361	941.7361	1049.774	1049.774
32	1004.111	1004.111	1119.626	1119.626
33	1068.486	1068.486	1191.728	1191.728
34	1134.861	1134.861	1266.080	1266.081
35	1203.236	1203.236	1342.682	1342.683
36	1273.611	1273.611	1421.534	1421.535
	(N = 4)		(N = 5)	
27	869.6439	869.6439	941.0682	941.0683
28	936.8227	936.8227	1014.358	1014.358
29	1006.501	1006.502	1090.398	1090.398
30	1078.680	1078.680	1169.188	1169.188
31	1153.359	1153.359	1250.727	1250.728
32	1230.538	1230.538	1335.017	1335.019
33	1310.217	1310.220	1422.057	1422.059
34	1392.395	1392.396	1511.847	1511.849
35	1477.074	1477.075	1604.387	1604.389
36	1564.253	1564.254	1699.676	1699.679
	(N = 8)		(N = 9)	
27	1130.650	1130.651	1185.556	1185.556
28	1221.233	1221.236	1281.540	1281.540
29	1315.316	1315.320	1381.274	1381.275
30	1412.899	1412.905	1484.758	1484.761
31	1513.982	1513.990	1591.992	1591.997
32	1618.566	1618.575	1702.976	1702.983
33	1726.649	1726.661	1817.710	1817.719
34	1838.232	1838.246	1936.194	1936.206
35	1953.315	1953.332	2058.428	2058.443
36	2071.898	2071.918	2184.412	2184.430

(*) HF-values are taken from REF.(6).

The above observations strongly suggest that EQUATION 10 is an exact representation of the high-Z asymptotical behaviour of the Hartree-Fock energies. In the following SECTION, we shall prove that it is indeed the case. It will be done by examining our energy expression in the context of the Z^{-1} perturbation approach to the isoelectronic series problem.

3. AN ALTERNATIVE FORM OF THE ENERGY EXPRESSION

Much of the work concerning the Z dependence of the total binding energy has developed from the Z^{-1} perturbation theory of Hylleraas [8]. The Z^{-1} perturbation expansion results in the following energy expression:

$$E(Z;N) = \Sigma C_i(N) Z^{2-i} \qquad (11)$$

The expansion coefficients are, in general, not known except for $C_0(N)$ which is the zero-order energy corresponding to a system of N noninteracting electrons about a nucleus of unit charge. The direct calculation of $C_i(N)$ for $i \geq 1$ is a non-trivial problem and its complexity rapidly increases with the number of electrons and with the order of the coefficient [9]. An easy way around is to calculate the energies of some members of an isoelectronic sequence, where all the coefficients $C_i(N)$ are fixed, and use this data to find their numerical values. This idea has been applied by Tal and Bartolotti [10] in reference to the Hartree-Fock energies of atomic systems with $N = 2,3,\ldots,86$ and $Z = N, N+1,\ldots,N+20$. By means of the least squares procedure, the authors have calculated $C_1(N)$, $C_2(N)$, k, l, $C_k(N)$ and $C_l(N)$ for the five-term truncated expansion. As the resulting energy formula appears to be highly accurate, the values of these coefficients can be taken as the reliable basis for the subsequent considerations.

Let us now proceed to show that EQUATION 10 is, in a way, consistent with the Z^{-1} perturbation expansion.

Indeed, as it follows from EQUATION 11, for sufficiently large atomic numbers, the total energy tends to be a quadratic function of Z:

$$E(Z;N) \cong C_0(N)Z^2 + C_1(N)Z + C_2(N). \qquad (12)$$

On the other hand, EQUATION 10 can be written in the analogous form:

$$E(Z;N) = (Y/2)Z^2 + [E(Zo+1) - E(Zo) - (Y/2)(1+2Zo)]Z + \{E(Zo) - [E(Zo+1) - E(Zo)]Zo + (Y/2)(Zo+Zo^2)\}. \qquad (13)$$

What is left to be done is to make sure that the following relations hold true:

$$C_0(N) = Y(N)/2 \qquad (14)$$

$$C_1(N) = \lim [E(Zo+1) - E(Zo) - (Y/2)(1+2Zo)] \qquad (15)$$

$$C_2(N) = \lim \{E(Zo) - [E(Zo+1) - E(Zo)]Zo + (Y/2)(Zo+Zo^2)\}, \qquad (16)$$

where the limits are taken for Zo tending towards infinity.

Since $C_0(N) = -2^{-1}\Sigma n_i^{-2}$, where n_i is the principal quantum number of the ith electron, the first relation can readily be proved by making a simple comparison. Thus, for example, when the ground state configuration $1s^2 2s^2$ is concerned (N = 4), $C_0(4) = -(1+1+1/4+1/4)/2 = -10/8$. From EQUATION 4 we find $Y(4)/2 = -(6 + 4)/8 = -10/8$.

Before proving the remaining two relations, it should be mentoned that the Hartree-Fock data [6] we have at our disposal are limited by Zo ≤ 36 (it is quite a long way to "infinity"). In principle, therefore, EQUATIONS (15) and (16) can hardly be expected to give us the exact values of $C_1(N)$ and $C_2(N)$. It turns out, however, that the right hand sides of these equations converge sufficiently fast, so that it is possible to get quite satisfactory results. The numerical values of $C_1(N)$ and $C_2(N)$ are displayed in TABLE 4.

TABLE 4. Comparison of $C_1(N)$ and $C_2(N)$ predicted from EQS.(15) and (16) with the literature values

N	$C_1(N)$		$C_2(N)$	
	EQ.(15)	TB	EQ.(16)	TB
2	0.625	0.62499	-0.111	-0.11093
3	1.023	1.02294	-0.357	-0.35865
4	1.571	1.57135	-0.814	-0.81703
5	2.335	2.33529	-1.739	-1.73853
6	3.262	3.27397	-3.123	-3.15109
7	4.355	4.38731	-5.052	-5.15647
8	5.664	5.67530	-7.882	-7.85628
9	7.138	7.13788	-11.398	-11.3519
10	8.776	8.77503	-15.833	-15.7446

TB-values are taken from the work by Tal and Bartolotti [10]

Taking into account that the parameters determined by the least squares method (those denoted by TB) suffer from being intercorrelated and, what is more, their numerical values are influenced by the number of terms in a truncated perturbation expansion, the results presented in TABLE 4 leave no room for doubt that EQUATIONS (15) and (16) stand for the exact representation of $C_1(N)$ and $C_2(N)$ respectively.

In this connection, some important by-products of our argument should be exposed. First of all, EQUATIONS (15) and (16) clearly reveal the physical meaning of the perturbation expansion coefficients $C_1(N)$ and $C_2(N)$. Secondly, these quantities are seen tc be related to each other in an explicit way. It is interesting to note, for example, that $C_1(N) = -\lim (\partial g/\partial Zo)$, where $g = g(Zo;N)$ denotes the right hand side of EQUATION 16.

Perhaps the most important observation is that, as it follows from EQUATION 15, the difference $E(Zo+1) - E(Zo)$ tends to be linear in Zo. This difference can be therefore replaced by the ordinary derivative dE/dZo if only Zo is sufficiently large. It would mean that, according to the Hellmann-Feynman theorem, $E(Zo+1) - E(Zo) = V_{ne}(Zo)/Zo$. It then follows that $E(Zo) - [E(Zo+1) - E(Zo)]Zo = T(Zo) + V_{ee}(Zo)$, where T stands for the kinetic energy of the electronic system.

Consequently, EQUATION 13 can now be written as

$$E(Z;N) = (Y/2)Z^2 + [V_{ne}(Zo)/Zo - (Y/2)(1+2Zo)]Z + [T(Zo) + V_{ee}(Zo) + (Y/2)(Zo+Zo^2)]. \qquad (17)$$

The advantage of this energy expression over the one given by EQUATION 13 consists in the fact that the Z-dependence of the Hartree-Fock energy is now entirely determined by the energy components of a single member of an isoelectronic sequence.

Finally, let us note that for the particular case of Z=Zo, EQUATION 17 leads to the fundamental physical relation:

$$E(Zo;N) = T(Zo;N) + V_{ne}(Zo;N) + V_{ee}(Zo;N). \qquad (18)$$

4. CONCLUDING REMARKS

The key result of this contribution consists in finding that $E(Z+2;N) - 2E(Z+1;N) + E(Z;N)$ converges to the limit $Y(N)$. This leads to the series of recurrence relations for the HF energies of isoelectronic systems. The resulting energy formula appears to be extremely accurate for systems with $Z > Zo(N)$. This formula is then proved to be the exact asymptotic representation of the Hartree-Fock total energies of N-electron atomic systems in their isoelectronic sequences. As a consequence, the first and the second order perturbation expansion coefficients are explicitely expressed in terms of the well defined physical quantities. It should be finally remarked that all the results presented are very simple and, what is more important, can easily be extended for the higher-N isoelectronic series.

ACKNOWLEDGMENTS

It is the author's pleasure to thank the Referee for his constructive criticism and very helpful suggestions.

REFERENCES

1. H. Margenau and G.M. Murphy (1959). "The Mathematics of Physics and Chemistry", Van Nostrand. Princeton; A.S. Davydov (1965). "Quantum Mechanics". Addison-Wesley, Reading, Massachusetts.
2. Sydney G. Davison (1969). "Atomic Structure", **Physical Chemistry**, An Advanced Treatise, Vol.III, Academic Press, New York/London.
3. C.L. Pekeris (1958). Phys. Rev. **112**, 1649; C.L. Pekeris (1959). Phys. Rev. **115**, 1216; C.L. Pekeris (1962). Phys. Rev. **126**, 143, 1470.
4. T. Kinoshita (1957). Phys. Rev. **105**, 1490; T. Kinoshita (1959). Phys. Rev. **115**, 336.
5. E. Clementi and C. Roetti (1974). Atomic Data and Nuclear Data Tables **14**, 177.
6. S. Fraga, J. Karwowski and K.M.S. Saxena (1976). "Handbook of Atomic Data", Elsevier SPC, Amsterdam/Oxford/New York.
7. D.R. Hartree (1968). "Numerical Analysis", Oxford University Press, Oxford.
8. E.A. Hylleraas (1930). Z. Phys. **62**, 209.
9. J. Midtal (1965). Phys. Rev. **138**, 1010; R.E. Knight (1969). Phys. Rev. **183**, 45; R. Snyder (1972). J. Phys. B **5**, 147.
10. Y. Tal and L.J. Bartolotti (1982). J. Chem. Phys. **76**, 4056.