NON-ORBITAL APPROACH TO MANY ELECTRON ATOMIC SYSTEMS. A FINITE
DIFFERENCE EQUATION FOR THE GROUND STATE ENERGY OF SYSTEMS IN
THEIR ISOELECTRONIC SERIES

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Abstract

A purely statistical approach to N-electron mononuclear sys-
tems is presented. The entropy-like functional of the elec-
tronic structure ("λ representation") turns out to inter-
relate the total energies of isoelectronic atoms and ions.
The resulting "combinatorial formula" for energies reprodu-
ces the corrected Hartree-Fock data with the error about 25
ppm. The physical interpreatation of the representation re-
mains as an open question.

1. Introduction

The shape of the present day quantum chemistry seems to be
mostly formed by the notion of atomic and molecular orbitals
based on the independent particle model. The concept of the
orbitals, however, is but an approximation and, strictly spea-
king, orbitals do not exist [1]. Such terms as hydrogen-like
orbitals, self-consistent field orbitals, natural orbitals,
the Slater or Morse or Gauss orbitals do not stand for the
real physical phenomena; they are only artifacts of the app-
roximation used in the calculations. The dilemma stems from
the fact that, in general, the Schrödinger equation cannot be
solved exactly, and some approximation methods must be intro-
duced.

A 50 years old approximation - the Hartree-Fock method in
its Roothaan form - is at present the most efficient technique
for solving many electron problems in terms of atomic and mo-
lecular orbitals [1,2]. The main disadvantage of this method

is the fact that the remaining small error in energy is still too large as compared to chemical energy changes. The absolute value of the error is of the same order of magnitude as the quantity which we would like to compute. So that, even if the Hartree-Fock functions are excellent approximations to the correct wave functions, they cannot provide quantitative agreement for the calculation of binding energies and related quantities. The so-called corrected Hartree-Fock energies (those with the total relativistic correction) are believed to be much closer to the experimental data (they are for $Z \leqslant 20$), but still they are affected by the neglect of two corrections, namely the effect of the finite size of the nucleus and the correlation energy [3,4].

Going beyond the Hartree-Fock method one would apply the so-called configuration-interaction method, but it generally takes a large number of configurations (a hundred or so terms) to give a truly satisfactory wave function. Not only it requires an enormous amount of computations, but also, and what is quite important, the correspondence between orbitals and electronic structure vanishes [5,6]. In short, the concept of the electron orbital as a wave function which describes one electron independently of any others, is principally incorrect if there is more than one electron [7].

Recently [8] we have introduced the concept of the so--called λ representation of atomic structure, and reported some preliminary results concerning the ground state energy of atoms and their k-positive ions arranged according to the generalized Periodic Table criterion. It turns out that the total energy of atomic systems arranged that way is the linear function of ZI_r, I_r being the relative information content — a functional related to our representation. We have also found that this function is, in some way, compatible with the energy expression [9] based on the Thomas-Fermi model. In the second part of our work [10], we started to examine the entropy dependence of the ground state energy for isoelectronic series. The key result presented there is the four-parameter energy formula the limiting behaviour of which exhibits consistency

with the Z^{-1} perturbation expansion model.

The aim of this note is to propose a modified form for the energy expression in which only three parameters are involved. This essential modification is based on the observation that the initial finite difference equation can be reduced in its order. To make this article self-contained, we recapitulate here the relevant notions of the λ representation; the novelty is only in the method of the exposition.

2. Definition of the "λ Representation"

In this Section we introduce a combinatorial mathematical structure generated by the coupled sets of initial elements, that is, of electrons and protons in the atomic system. As it follows from the Schrödinger equation, the Hamiltonian of an atomic system

$$H = \sum_{i=1}^{N} \left(-\nabla_i^2/2 - Z/r_i \right) + \sum_{i=1}^{N} \sum_{j>i} 1/r_{ij} \qquad (1)$$

depends on the numbers N and Z only

$$H = H \left(\cdot \ ; \ N, \ Z \right), \qquad (2)$$

N and Z being the cardinalities of the sets of electrons, E , and protons, P , in the system:

$$\text{card} \left(E \right) = N, \ \text{card} \left(P \right) = Z. \qquad (3)$$

Therefore the structure of the system is, in principle, entirely determined by the numerical values of the integers N and Z. Because the sets E and P are known to be physically related, one might suspect that the system structure has something to do with some binary relations in the cartesian product $E \times P$. By a technique of a free association, we anticipate these relations will be functions $f: E \rightarrow P$. In general, for $N \neq Z$, we do not expect these functions to be one-to-one; we shall just consider them as all possible mappings from the set $E = \{e_1, e_2, \ldots e_N\}$ to the set $P = \{p_1, p_2, \ldots, p_Z\}$.

Given N and Z, we first note that any function f defines some partition of E simply by $f^{-1}(p_j) \subset E$, $p_j \in P$.

Thus, for instance, in the case of $N = 3$ and $Z = 4$, the func-
tions f_1, f_2 and f_3

$$(4)$$

$$(f_1) \qquad\qquad (f_2) \qquad\qquad (f_3)$$
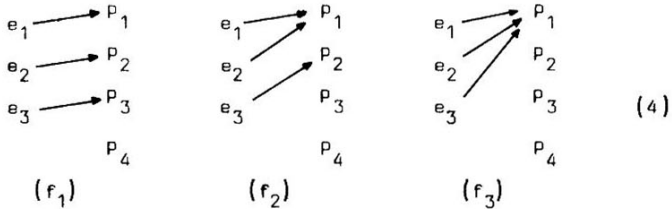
define the respective partitions of E: $\{\{e_1\}, \{e_2\}, \{e_3\}, \{\emptyset\}\}$,
$\{\{e_1, e_2\}, \{e_3\}, \{\emptyset\}, \{\emptyset\}\}$ and $\{\{e_1, e_2, e_3\}, \{\emptyset\}, \{\emptyset\}, \{\emptyset\}\}$.
By inspection of this function diagram, we also see that each
function f defines the corresponding partition of P determined
by the number of arcs which reach the vertices of the codomain
of f. In our example, the respective partitions of P are the
following: $\{\{p_1, p_2, p_3\}, \{p_4\}\}$, $\{\{p_1\}, \{p_2\}, \{p_3, p_4\}\}$ and $\{\{p_1\}, \{p_2, p_3, p_4\}\}$.

    With this in mind, we shall now take into account the
physical principle of indistinguishability of electrons, and
the same principle regarding protons. These principles suggest
that some mappings f will be physically equivalent, so that
the set $F = \{f \mid f : E \longrightarrow P\}$ can be split into the classes of in-
distinguishable functions. Referring to the function diagram
(4), we see that f_1, f_2 and f_3 would belong to the different
equivalence classes in F. Regarding partitions of E and P,
the particle identity principle imposes us to replace each
subset in the respective partition by its cardinality:

function	E-partition	P-partition	
f_1	(1,1,1,0)	(3,1)	
f_2	(2,1,0,0)	(2,1,1)	(4′)
f_3	(3,0,0,0)	(3,1)	

We see that the partitions of E exhaust all possible partit-
ions of the number $N = 3$ into $Z = 4$ non-negative integers. We
also observe that partitions of P are dual to those of E in
the sense that their components are equal to the number of
repetitions in the E-partitions.

Example $(4,4')$ offers a general rule for splitting F into the equivalence classes of indistinguishable functions $f:E \rightarrow P$. Given card $(E) = N$ and card $(P) = Z$, let λ denote a partition of N into Z non-negative integers

$$\lambda = (n_1, n_2, \ldots, n_Z) ; \quad \sum n_i = N ; \quad n_i \geqslant n_j \quad \text{for } j > i \quad (5)$$

A partition $\tilde{\lambda}$ of the integer Z

$$\tilde{\lambda} = (r_1, r_2, \ldots, r_q) ; \quad \sum r_k = Z \quad (6)$$

we shall call dual of λ if r_k are the subsequent numbers of the repetitions in the sequence of n_i. From the preceding discussion it then follows that the pair $(\lambda, \tilde{\lambda})$ univocally describes the respective equivalence class of mappings $f:E \rightarrow P$. However, since $g: \lambda \rightarrow \tilde{\lambda}$ is a well defined function, two mappings f and $f' \in F$ will be equivalent if only they correspond to the same partition λ (5). The class of mappings f defining the same partition λ will be denoted F_λ.

We now want to determine the number $W(\lambda)$ of functions f in each class F_λ, i.e., $W(\lambda) = \text{card}(F_\lambda)$. One way of dealing with this problem is to interpret λ as a particular distribution of N identical objects in Z identical cells. From simple combinatorics it then follows [11] that

$$W(\lambda) = N! Z! \left(\prod n_i! \times \prod r_j! \right)^{-1} \quad (7)$$

Moreover, since card $(F) = Z^N$, the cardinalities of F_λ now define the "probabilities" of λ as

$$P(\lambda) = W(\lambda) Z^{-N}$$
$$\sum p(\lambda) = 1 \quad (8)$$

Consequently, the family (lattice [12]) $\Lambda = \{\lambda_1, \lambda_2, \ldots, \lambda_L\}$ of all defferent partitions (5), equipped with the probability measure (8), forms the probability space

$$(\Lambda, \lambda ; p) \quad (9)$$

of all mappings $F = \{f \mid f:E \rightarrow P\}$ subdivided into L equivalence classes F_λ of indistinguishable functions. The probability distribution P (EQS. 7,8) is induced here by nature of the particle identity principle, and the space itself is genarated exclusively by N and Z - the cardinalities of E and P.

It is our idea to consider the space just defined as a sort
of statistical model (representation) of the atomic structure.
In its spirit, this idea seems to be closely connected both
with the Loge Theory [13] and the Information Theory [14] app-
roaches to many electron problems. The point is that the state
of an electronic system is, in each case, associated with the
"leading event" in the respective probability space. The essen-
ce of our approach is that the ground state of an atomic system,
specified by N and Z, is represented by this partition λ for
which the corresponding class F_λ of functions $f: E \longrightarrow P$ is most
numerous $\left(\text{card}(F_\lambda) = W(\lambda) = \max\right)$, that is, by the one for which
$P(\lambda) = \max$. Referring again to our current example $(4, 4')$, we
have

function class, F_λ	$W(\lambda)$, EQ.7	$P(\lambda)$, EQ.8	
$(1,1,1,0)$	24	0.3750	
$(2,1,0,0)$	36	0.5625	$(4'')$
$(3,0,0,0)$	4	0.0625	

Thus, according to our idea, this case of N = 3 and Z = 4
would correspond to the ground state of Be^+, represented by
the partition $\lambda = (2,1,0,0)$.

As for some integers N and Z the probability $P(\lambda)$ may
have an improper maximum for more than one partition, the above
symbolic representation can be degenerate. For example, in the
case of the nitrogen ion N^+ (N=6, Z=7) there are two partit-
ions $(2,2,1,1,0,0,0)$ and $(2,1,1,1,1,0,0)$ with the same maximum
probability equal to 0.321295 (EQS.7,8). Nevertheless, the
partition (5) which maximizes the expression (7) we shall call
the "λ representant", and, in general, the image

$$(N,Z) \rightarrow (\Lambda, \lambda; P) \tag{10}$$

will be referred to as the "λ representation" of the corres-
ponding atomic system in its ground state.

We therefore anticipate a more or less pronounced relat-
ionship between the physical properties of atomic systems,
$A(N,Z)$, and the mathematical features of $(\Lambda, \lambda; P)$.

In order to express physical quantities of $A(N,Z)$ in terms
of the λ representation, we shall need some functionals

related to the probability space $(\bigwedge, \lambda; P)$. The most appropriate seem to be those borrowed from the well established theories [15]

$$S = \ln W_{max} \qquad \text{entropy-like}$$
$$I = -\ln P_{max} \qquad \text{amount of information} \qquad (11)$$
$$H = -\sum_{\lambda} P(\lambda)\ln P(\lambda) \; \text{Shannon's function}$$

These functionals permit us to express the λ representation idea in more physical terms by stating that the ground state of an atomic system is characterized by the maximum "entropy" or, alternatively, by the minimum "amount of information".

Let us now turn our interest to the λ representants themselves. Because the number L of the equivalence classes depends rather strongly on N (for N≈30, L=5604), it is worth noting[10] that for N⩽Z = 2,3,...,33, the most probable partition of the natural number N into Z non-negative integers is of a general form

$$(\underbrace{\frac{n}{3,\ldots,3}}, \underbrace{\frac{m}{2,\ldots,2}}, \underbrace{\frac{l}{1,\ldots,1}}, \underbrace{\frac{k}{0,\ldots,0}}), \qquad (12)$$

where n = 0, 1, 2; m = 0, 1, ... , 7 (m⩾n) and, evidently, l = N - 3n - 2m and k = Z - N + 2n + m. Thus any λ representant can be identified by the pair (n,m) of two integers:

n	m	λ	
0	0	(1, ... ,1,0, ... ,0)	
0	1	(2,1, ... ,1,0, ... ,0)	
0	2	(2,2,1, ... ,1,0, ... ,0)	
...	...	...	(13)
1	1	(3,2,1, ... ,1,0, ... ,0)	
1	2	(3,2,2,1, ... ,1,0, ... ,0)	
...	...	...	

The mapping $(N,Z) \longrightarrow (n,m)$ is partly displayed in TABLE 1. This mapping can also be described algebraically. It results from the fact that the formula (7) applied for partitions (12) takes the explicit form

$$W_{max}(\lambda) = W(N,Z; n,m) =$$

$$= N!Z! \left[(3!)^n (2!)^m \, n!m! \, (N-3n-2m)! \times (Z-N+2n+m)! \right]^{-1} \quad (14)$$

Now, by comparing W_{max} for any two (or more) types of partitions, $W(N,Z; n,m) = W(N,Z; n',m')$, one can easily find the doubly (multiple) represented systems $A(N,Z)$. For example, the equality $W(N,Z; 0,1) = W(N,Z; 0,0)$ leads to the relation $N!Z!/2(N-2)!(Z-N+1)! = N!Z!/Z!(Z-N)!$, or simply $Z=(N(N+1)/2)-1$. Thus, if N and Z are related that way, the respective atomic systems $A(N,Z)$ are doubly represented by the $(0,1)$ and $(0,0)$-type of partitions. At the same time, these systems stand for the turning points between two types in the poset of the λ representants. Therefore, if $Z \geqslant N(N+1)/2$, the corresponding systems are represented by the $(0,0)$-type of partitions. In a similar way, one can describe any part of the whole map $(N,Z) \longrightarrow (n,m)$:

Z/N-relation	λ-type, (n,m)
$Z \geqslant N(N+1)/2$	$(0,0)$
$Z = N(N+1)/2-1$	$(0,0), (0,1)$
$N(N-1)/4-1/2 < Z < N(N+1)/2-1$	$(0,1)$
$Z = N(N-3)/6+1/3$	$(0,1), (0,2)$
$N(N-3)/6+1/3 < Z < N(N-1)/4-1/2$	$(0,2)$
$\cdots$	$\cdots$

$$(15)$$

The above construction of the λ representation is purely mathematical, and some possible linkages with physics are only of a formal nature. This is a serious deficiency in our model, because it makes physical interpretation very difficult. Nevertheless, we feel that an examination of this formal structure will be useful even when its physical justification is incomplete or unsatisfactory.

TAB.1. The mapping $(N,Z) \longrightarrow (n,m)$

Z \ N	3	4	5	6	7	8	9	10	11
3	0,1								
4	0,1	0,1							
5	0,1 0,0	0,1	0,1						
6	0,0	0,1	0,1	0,2					
7	0,0	0,1	0,1	0,1	0,2				
8	0,0	0,1	0,1	0,1	0,2	0,2			
9	0,0	0,1 0,0	0,1	0,1	0,2	0,2	1,1 0,3		
10	0,0	0,0	0,1	0,1	0,2 0,1	0,2	0,2	1,2 0,3	
11	0,0	0,0	0,1	0,1	0,1	0,2	0,2	0,3	1,2
12	0,0	0,0	0,1	0,1	0,1	0,2	0,2	0,3 0,2	1,2 0,3
13	0,0	0,0	0,1	0,1	0,1	0,1	0,2	0,2	0,3
14	0,0	0,0	0,1 0,0	0,1	0,1	0,1	0,2	0,2	0,3
15	0,0	0,0	0,0	0,1	0,1	0,1	0,2	0,2	0,3 0,2
16	0,0	0,0	0,0	0,1	0,1	0,1	0,2	0,2	0,2
17	0,0	0,0	0,0	0,1	0,1	0,1	0,2	0,2	0,2
18	0,0	0,0	0,0	0,1	0,1	0,1	0,1	0,2	0,2
19	0,0	0,0	0,0	0,1	0,1	0,1	0,1	0,2	0,2
20	0,0	0,0	0,0	0,1 0,0	0,1	0,1	0,1	0,2	0,2
21	0,0	0,0	0,0	0,0	0,1	0,1	0,1	0,2	0,2
22	0,0	0,0	0,0	0,0	0,1	0,1	0,1	0,2 0,1	0,2
23	0,0	0,0	0,0	0,0	0,1	0,1	0,1	0,1	0,2

3. Isoelectronic Series Problem

Now we must precise what is meant by saying that the λ representation reflects the ground state of many electron atomic systems. Since the total energy E is one of the most fundamental properties of atoms and ions, it would then be important to state a possibility of expressing E in terms of our representation. To proceed with the program of determining $E(Z;N)$, the energy of atomic systems with fixed number N of electrons and varying number Z of protons, let us consider the auxiliary quantity

$$D_1 = \Delta(-E/Z)/\Delta S \qquad (16)$$

where E/Z is the total energy per single proton, $S = \ln W_{max}$ stands for the previously (EQ.11) defined entropy-like functional of the corresponding λ representant, and

$$\Delta(-E/Z) = |E(Z+1; N)/(Z+1) - E(Z; N)/Z| \qquad (17)$$

$$\Delta S = S(Z+1; N) - S(Z; N) \qquad (18)$$

Taking the corrected Hartree-Fock energies, E_{CHF}, as the basis for the computations [4], let us next examine the function u: $Z \rightarrow D_1$. Mainly for considerations of space, we shall here confine ourselves to picture only the cases of N=6 and N=7 (FIG.1). As it is seen, the plots D_1 vs. Z reveal some singularities which (TAB.1, EQ.15) appear to correspond exactly to the doubly represented systems, namely N^+, Ca^{14+}, Ne^{3+} and Co^{19+}. The respective plots for N=3,4,...,13 show that in each case of isoelectronic series under study, the λ representation degeneracy invariably manifests itself by singularities of the function u: $Z \rightarrow D_1$. Another permanent feature of these plots is that, for singly represented systems, D_1 appears to be highly regular function of Z. Since the total energy is involved in D_1, the above observations make clear the physical meaning of the λ representation classification and, by the same, make the representation idea plausible itself.
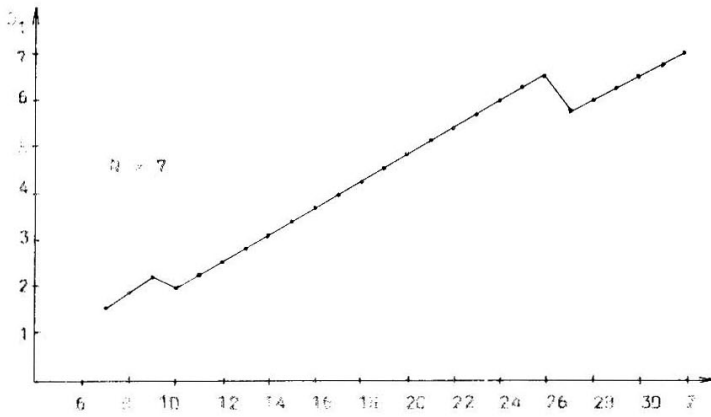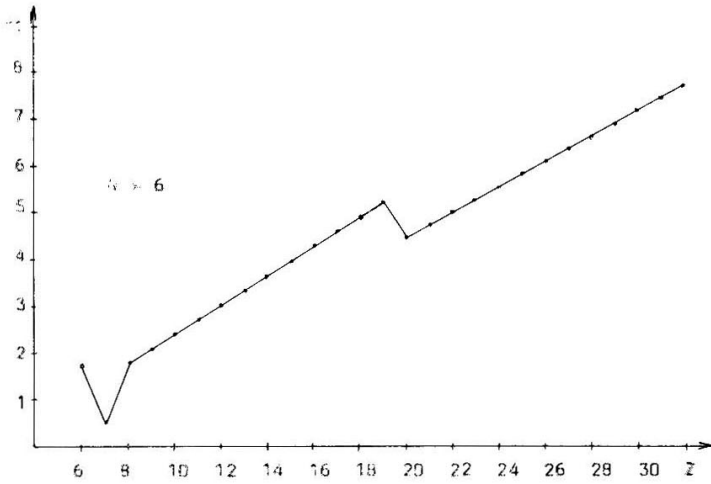
Fig. 1. σ_k plotted vs. Z for $N = 6$ and 7

Judging from the plots like those in FIG.1, one might re-
cognize D_1 as simply linear function of Z. Numerical examina-
tions, however, reveal some curvature which, being scarcely
appreciable for $N > 5$, becomes almost visible for the lower-N
cases. It is difficult to say, but the latter feature seems to
be partly explained by the fact that the λ representation is
the statistical concept applied for the reather small particle
numbers, so that some more or less diffused limit of its re-
liability can exist. In any case, one may try to remove the
curvature in question by introducing a quadratic term into
Z-dependence of D_1, and then get the relation

$$\Delta(-E/Z) = D_1 \Delta s, \tag{19}$$

where now

$$D_1 = D_1(Z; N, \lambda) = d_0(N,\lambda) + d_1(N,\lambda)Z + d_2(N,\lambda)Z^2 \tag{20}$$

d_2 being expected to be very small as compared with d_1.

This is, of course, just a finite difference equation
relating the increment of $-E/Z$ to the entropy increment. The
analytical form for the energy expression can be therefore
obtained simply by "integrating" EQ.19, that is, by carrying
the summations

$$\Sigma \Delta s, \qquad \Sigma Z \Delta s \qquad \text{and} \qquad \Sigma Z^2 \Delta s \tag{21}$$

It can easily be done by considering the entropy definition
(EQ.11) in combination with EQ.14. Applying then EQ.18, one
gets the explicit formula for the entropy increment

$$\Delta S = \ln(Z + 1)/(Z - N + 2n + m + 1) \tag{22}$$

With this basis, the calculation of the sums (21) becomes
almost self-evident, so that we can immediately write our key
result in the form

$$-E(Z; N, \lambda) = \left[-E_0/Z_0 + \sum_{i=0}^{2} d_i \left(\sum_{\alpha=0}^{Z-Z_0-1} \alpha^i \ln Y_\alpha \right) \right] \times Z \tag{23}$$

where

$$Y_\alpha = Y(\alpha; Z_0, N, m, n) = (Z_0 + 1 + \alpha)/(Z_0 - N + 2n + m + 1 + \alpha) \tag{24}$$

Z_0 being the atomic number of the first system in the
sequence in which the summations (21) go over, and $E_0 = E(Z_0)$.

With EQUATION (23) we have got total energy of isoelectro-
nic systems related to their λ representants, the latter being
determined here by the values of n and m. This equation, however
is, in a way, just a semi-empirical formula in which three para-
meters d_0, d_1 and d_2 are involved. Thus, to examine the correc-
tness of our energy expression, it is necessary to find the d_i-
-values for each sequence of N-electron systems represented by
the same type of partitions (13). Since we cannot do this by
means of any sort of "ab initio" computations, we are then for-
ced to employ the standard least-squares method.

Let us start from the case of N=7 electrons (FIG.1). Here
we have three series of systems represented by (0,2), (0,1)
and (0,0)-type of partitions, the last two of them being long
enough to perform the least-squares fits. Exluding the singul-
ar points of the function u: $Z \rightarrow D_1$, we choose Z_0=11 for the
(0,1)-type, and Z_0=28 for the (0,0)-type of the λ represent-
ants. Hence, according to EQ.24, $Y_\alpha = (12+\alpha)/(6+\alpha)$ and $Y_\alpha =$
$=(29+\alpha)/(22+\alpha)$ respectively. After having introduced these
quantities into EQ.23, and then fitting this equation to the
corrected Hartree-Fock data [4], one gets d_0= 2.29839 a.u.,
d_1=0,283886 a.u. and d_2=0.00008847 a.u. for the first series
and, respectively, 6.02134, 0.252455 and 0.0007278 for the se-
cond one. The comparison between the original data, E_{cHF}, and
those reproduced by EQ.23, E_λ, is presented in TABLE 2. It is
seen that the errors of E_λ are remarkably small; in the case
of (0,0)-represented systems one may even state that there is
no error at all. The mean absolute error is found to be 0.0134
a.u. for the (0,1)-series, and only 0.0008 a.u. for the (0,0)-
one; the respective mean relative errors are equal to 0.003%
and 0.00005%, or, simply, 30 ppm and 0.5 ppm.

The neuralgic point in discussing the accuracy of our ener-
gy expression is that there is also some intrinsic error in the
Hartree-Fock data themselves, apart from that of the unrelati-
vistic correlation energy. For example, applying the test of
the virial theorem, V.T., that predicts a value of -2 for the
ratio P.E./K.E. of the potential and kinetic energies [2], one
finds the relative error, $((V.T.+2)/2)10^6$, of the HF-SCF computa-

TAB.2. Comparison of the corrected Hartree-Fock energies, E_{cHF}, and those reproduced by EQ.23, E_λ, for the 7-electron atomic systems.

All energies are in a.u..

(n,m)	Z	$-E_{cHF}$	$-E_\lambda$	Relative difference, %
	12	187.1485	187.1739	0.0136
	13	223.5272	223.5533	0.0117
	14	263.1926	263.2079	0.0058
	15	306.1503	306.1515	0.0004
	16	352.4064	352.3956	0.0031
	17	401.4677	401.9505	0.0043
(0,1)	18	454.8419	454.8235	0.0040
	19	511.0358	511.0232	0.0025
	20	570.5591	570.5559	0.0006
	21	633.4198	633.4278	0.0013
	22	699.6277	699.6445	0.0024
	23	769.1929	769.2113	0.0024
	24	842.1253	842.1322	0.0008
	25	918.4361	918.4137	0.0024
	29	1257.699	1257.700	0.0001
	30	1351.084	1351.084	0.0000
	31	1447.923	1447.922	0.0001
(0,0)	32	1548.231	1548.230	0.0001
	33	1652.022	1652.022	0.0000
	34	1751.313	1759.313	0.0000
	35	1870.118	1870.119	0.0001
	36	1984.456	1984.455	0.0001

tions coming up to 13.7 ppm in the relatively simple case of
the two-electron atomic system F^{7+}. This error is of the same
order as that of our regression equation.

To complete the discussion of how well this equation is
fitting, let us also examine the residual mean squares RMS- a
measure of variance, and the multiple correlation coefficient
squared MCCS. In our current example, we find RMS = $3.39 \cdot 10^{-4}$
and MCCS = 0.99999999 for the $(0,1)$-case, and, respectively,
$1.4 \cdot 10^{-6}$ and 0.999999999999 for the $(0,0)$-one. Since MCCS-value
represents the fraction of the total variation of E accounted
for by the fitted equation, the result reported tells us that
the total variability of the energy is modeled by EQ.23 at
least in 99.999999% or, equivalently, at most 0.000001% of the
total sum of squares is left to be explained.

We are now prepared to extend the examination of EQ.23 to
the other cases of isoelectronic series. The aim of these stu-
dies is to prove that our energy expression keeps to be remar-
kably accurate for as many as fourteen N-electron sequences,
$(N = 5,6,\ldots,13)$, distinguished by the different types of the
λ representants involved. The results of fitting EQ.23 to the
corrected Hartree-Fock data are summarized in TAB.3.

As it is seen, the variance (RMS) keeps within the bounds
of the 10^{-4} level with only one exception for the case of N=8
electrons. Apart from the case of the rather short series of
5-electron systems $(d.f.=5)$, the MCCS-values are invariably
higher than 0.99999999. The averaged mean absolute error, equal
to about 0.01 a.u. or, equivalently, 0.27 eV (6.7 kcal/mol),
makes our equation nearly satisfactory even from the chemical
point of view. Finally, the averaged mean relative error, equal
to 25 ppm (0.0025%), is nearing the error limit of the Hartree-
-Fock approximation itself.

TAB.3. The results of fitting EQ.23 to the corrected
       Hartree-Fock data (Ref.4).

N	(n,m)	Z_0	Z_{max}	MRE	RMS	MCCS
5	$(0,1)$	5	13	142	$2.08(-4)$	0.99999996
	$(0,0)$	15	36	35	$8.21(-4)$	0.999999996
6	$(0,1)$	8	18	46	$1.24(-4)$	0.999999992
	$(0,0)$	21	36	5	$6.42(-5)$	0.999999999
7	$(0,1)$	11	25	30	$3.39(-4)$	0.999999994
	$(0,0)$	28	36			
8	$(0,1)$	14	34	35	$2.06(-3)$	0.999999991
9	$(0,1)$	11	27	13	$4.46(-4)$	0.999999998
10	$(0,2)$	13	19	6	$1.91(-5)$	0.999999999
	$(0,1)$	23	36	4	$5.80(-5)$	0.9993999998
11	$(0,2)$	16	25	8	$6.78(-5)$	0.9999999991
	$(0,1)$	28	36	0.5	$2.28(-6)$	0.99999999998
12	$(0,2)$	19	31	8	$1.34(-4)$	0.9999999991
13	$(0,2)$	22	36	8	$2.41(-4)$	0.9999999992

MRE - mean relative error, ppm
RMS - residual mean squares
MCCS - multiple correlation coefficient squared

4. Concluding Remarks

Details having already been discussed in the appropriate sections (see also Ref. 8,10), we wish to bring out here only the main points of the results presented.

Equation (23) introduces a particular dependence on Z in the total energy of N-electron atomic systems. What is most important is that, to say nothing of the surprising accuracy, the explicit form of this energy-entropy relation is rigorously defined by the type of the corresponding λ representants. In other words, the classification of atomic systems according to the different forms of their λ representants appears to be essential for the quality of Eq.23. It might be argued that this feature is to some extent arbitrary, and that any mathematician could construct simpler functions that were just as suggestive. To this we can only reply that we were led to our equation by the independent idea of the λ representation itself. On account of this, without pretending to have a definite answer to a problem of the physical interpretation whose difficulty can scarcely be measured, we venture to suggest that this idea, after being subsequently scrutinized, may be helpful in understanding the collective behaviour of the electrons present in the atomic systems.

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