Theoret. chim. Acta (Berl.) 28, 363–390 (1973)

SCF Dirac-Hartree-Fock Calculations in the Periodic System

I. Calculated Ground States of All Elements from $Z=1$ to $Z=120$

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Received August 10, 1972

Using the Dirac-Hartree-Fock (DHF) program which includes the exchange terms for electrostatic interactions, the Dirac equation was solved numerically by UNIVAC computer for all elements with $Z=1-120$. A solution was performed for each element of the periodic system in several electronic configurations, to obtain the configuration with lowest total energy as the calculated ground state.

Mit Hilfe des Dirac-Hartree-Fock-(DHF)-Programms, das die Austauschterme für elektrostatische Wechselwirkungen einschließt, wurde die Dirac-Gleichung für alle Elemente mit $Z=1-120$ numerisch (UNIVAC-Rechenanlage) gelöst. Die Rechnung wurde für jedes Element des Periodensystems in verschiedenen Elektronenkonfigurationen durchgeführt, um die Konfiguration mit der tiefsten Gesamtenergie für den Grundzustand zu erhalten.

En utilisant un programme Dirac-Hartree-Fock (DHF) comportant les termes d'échange de l'interaction électrostatique, l'équation Dirac a été résolue numériquement avec un ordinateur UNIVAC, pour tous les éléments de $Z=1$ à 120. Les calculs ont été developpés pour plusieurs configurations électroniques de chacun des éléments de la classification périodique afin de déterminer celle dont l'énergie est la plus basse, qui correspond à l'état fondamental.

1. Introduction

During the last decade seceral complete self-consistent Hartree or Hartree-Fock calculations were performed of ground states and eigenvalues of all elements in the periodic system. First, non-relativistic calculations in one (NRHFS) [1] or several electron configurations (NRH) [2] were done and then non-relativistic Hartree-Fock (NRHF) calculations [3 and 4] (in one configuration for each Z) or approximative (NRHF) calculations using the wave function from NRH calculations [2] were performed in several electron configurations for each element. However, all NRH or NRHF results neglected relativistic effects and gave very inaccurate values of eigenvalues and total energies for all heavier atoms.

The only systematic relativistic calculations, which use Slater approximation for the exchange potential (Dirac-Fock-Slater-DFS), were performed for all elements from $Z=2-101$ in one accepted electron configuration [5–7]. These calculations were recently extended in the heavy elements region in several electron configurations (for $Z=104-132$), using the non-modified Slater exchange potential [8], or very recently for the region $Z = 89 - 172$, using 2/3 of the usual Slater exchange potential [9] as the exchange term in the Dirac equation.

More exact than DFS, the relativistic Hartree-Fock solution of the Dirac equation (Dirac-Hartree-Fock-DHF) including the exact form of the exchange terms as formulated by Grant [10 – 12], was rarely performed and then only for a few atoms [13 – 16]. Recently, DHF calculations have been extended for a few elements through the entire periodic system [17, 18] and thoroughly in several configurations for 118 – 131 elements [19]. No systematic calculations (DHF) of ground states of all elements in the periodic system, in reveral configurations for each element, was yet published. The aim of this work was to perform such calculations in the region from $Z = 1 - 120$, with the intent of testing the DHF method in the known region of the periodic system. Such results should be valuable for future calculations of ionization potentials in less known regions (as e.g. in actinide and lanthanide series) or in the unknown region, around 110 – 114 elements [20], where some very stable isotopes are predicted to exist and could, perhaps, be found in nature.

2. Method of Calculation

2.1. Formulae Used in Calculations

In our calculations we used the formulae derived by Swirles [21] and Grant [10 – 12]. Following Grant's notation in [10] we used the following schema (denoting index k of Grant as $\bar{\mathrm{j}}$): Dirac-Hamiltonian $\boldsymbol{H}_{\mathrm{D}}$ for many-electron atoms (in central field approximation) was defined in atomic units as:

$$\boldsymbol{H}_{\mathrm{D}} = \sum_{\bar{j}} \boldsymbol{h}_{\bar{j}} + \tfrac{1}{2} \sum_{\overline{jl}} \boldsymbol{g}(\overline{jl}) \tag{1}$$

with Dirac-Hamiltonian for a single electron having number $\bar{\mathrm{j}}$ present in the atom as:

$$\boldsymbol{h}_{\bar{j}} = [ic\vec{\boldsymbol{\alpha}}(\bar{j})\boldsymbol{\nabla}_{\bar{j}} - \boldsymbol{\beta}(\bar{j})c^2 - V(r_{\bar{j}})]\,. \tag{2}$$

Here in (1) term $\frac{1}{2}\sum_{\overline{jl}} \boldsymbol{g}(\overline{jl})$ is the exchange term for interaction $\boldsymbol{g}(\overline{jl})$ of each $\bar{j}$ th electron with $\bar{l}$ th electron (each couple taken twice in Σ). In (2) the operators $\vec{\boldsymbol{\alpha}}$ and $\boldsymbol{\beta}$ are defined as matrices:

$$\vec{\boldsymbol{\alpha}} = \begin{pmatrix} 0 & \boldsymbol{\sigma}^p \\ \boldsymbol{\sigma}^p & 0 \end{pmatrix}, \quad \boldsymbol{\beta} = \begin{pmatrix} \boldsymbol{I} & 0 \\ 0 & -\boldsymbol{I} \end{pmatrix}. \tag{3}$$

where $\boldsymbol{I}$ is the unit 2 × 2 matrix and $\boldsymbol{\sigma}^p$ represents three Pauli matrices:

$$\boldsymbol{\sigma}_x^p = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_y^p = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_z^p = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{4}$$

The potential function $V(r_{\bar{j}})$ defines electrical potential on the nucleus. For description of the atom, one-electron functions are constructed:

$$\psi_{nkm}(r_{\bar{j}}) = \frac{1}{r_{\bar{j}}}\begin{pmatrix} \chi_{k,m} & P_{nk}(r_{\bar{j}}) \\ i\chi_{-k,m} & Q_{nk}(r_{\bar{j}}) \end{pmatrix} \tag{5}$$

which are eigenfunctions of operators $\boldsymbol{J}^2$, $\boldsymbol{S}^2$ and $\boldsymbol{J}_z$ and contain radial functions Q_{nk}, P_{nk} and angular functions $\chi_{k,m}$. These functions are defined as:

$$\chi_{k,m} = \sum_{\sigma=\pm\frac{1}{2}} C(l\tfrac{1}{2}j;\, m-\sigma, \sigma)\, Y_l^{m-\sigma}\phi_{\frac{1}{2}}^{\sigma} \tag{6}$$

where $C(l\frac{1}{2}j;\, m-\sigma, \sigma)$ denotes a Clebsch-Gordon coefficient for vector addition of two angular momenta, $Y_l^{m-\sigma}$ is a spherical harmonic and $\phi_{\frac{1}{2}}^{\sigma}$ is a spin eigenfunction, represented by column matrices for two possible values of σ ($+\frac{1}{2}$ or $-\frac{1}{2}$):

$$\phi_{\frac{1}{2}}^{\frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \phi_{\frac{1}{2}}^{-\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{7}$$

Function $\chi_{k,m}$ contains the relativistic quantum numbers k and a (a is sign of spin quantum number) instead of usual quantum numbers l, j present in Clebsch-Gordon coefficients:

$$k = -(j+\tfrac{1}{2})\,a \qquad a = \begin{cases} +1 \\ -1 \end{cases} \text{ or where } \quad j = l + \tfrac{1}{2}a\,. \tag{8}$$

The magnetic quantum number m can have all $2j+1$ values between $j, j-1, \ldots -(j-1), -j$. The main quantum number n is the same in both relativistic or non-relativistic theory.

For definition of one-electron function in the Dirac equation, four quantum numbers are used (n, j, m, a) or (n, k, m, a), related by (8), where only three quantum numbers (n, l, m) are used in non-relativistic Hartree-Fock method. Electron $\bar{j}$ or $\bar{l}$ with state A defined by four quantum numbers (n_A, j_A, m_A, a_A) or $(n_A, k_A, \mathrm{m}_A, a_A)$ is further abreviated by index A only, denoting all four quantum numbers.

Using the one-electron function (5) and Pauli exclusion principle the determinantial Hartree-Fock functions are constructed (as linear combination of products of functions (5)):

$$\phi = (N!)^{-\frac{1}{2}} \begin{vmatrix} \psi_1(A^1) & \ldots\ \psi_1(A^j) & \ldots\ \psi_1(A^N) \\ \vdots & \vdots & \vdots \\ \psi_i(A^1) & \ldots\ \psi_i(A^j) & \ldots\ \psi_i(A^N) \\ \vdots & \vdots & \vdots \\ \psi_N(A^1) & \ldots\ \psi_N(A^j) & \ldots\ \psi_N(A^N) \end{vmatrix} \tag{9}$$

where the list of $(A^1, \ldots, A^j, \ldots, A^N)$ defines the electron configuration of the atom.

For function ϕ the total energy E of the atom in the given electron configuration can be calculated by a usual quantum mechanical relation:

$$E = \int \phi^* \boldsymbol{H}_{\mathrm{D}}\, \phi\, d\tau \Big/ \int \phi^* \phi\, d\tau = \sum_{\mathrm{A}} I(\mathrm{A}) + \tfrac{1}{2} \sum_{\mathrm{A,B}} [J(\mathrm{A,B}) - K(\mathrm{A,B})] \tag{10}$$

In (10) the matrix elements $I(\mathrm{A})$ (Slater direct integrals) are obtained by multiplication:

$$I(\mathrm{A}) = \langle \mathrm{A}|\boldsymbol{h}_\mathrm{A}|\mathrm{A}\rangle = \int \psi_\mathrm{A}^* \boldsymbol{h}_\mathrm{A} \psi_\mathrm{A} dr \tag{11}$$

which, after integration leads directly to form:

$$\begin{aligned} I(\mathrm{A}) = c \int_0^\infty \Bigg\{ P_\mathrm{A} \left[\frac{dQ_\mathrm{A}}{dr} - \frac{k_\mathrm{A}}{r} Q_\mathrm{A} + \left(c - \frac{V}{c} \right) P_\mathrm{A} \right] \\ - Q_\mathrm{A} \left[\frac{dP_\mathrm{A}}{dr} + \frac{k_\mathrm{A}}{r} P_\mathrm{A} + \left(c + \frac{V}{c} \right) Q_\mathrm{A} \right] \Bigg\} dr \end{aligned} \tag{12}$$

The matrix elements of exchange interactions $J(\mathrm{A, B})$ and $K(\mathrm{A, B})$ in (10) have the form:

$$\begin{aligned} J(\mathrm{A, B}) &= \langle \mathrm{A, B}|\boldsymbol{g}|\mathrm{A, B}\rangle = \iint \psi_\mathrm{A}^*(1)\, \psi_\mathrm{B}^*(2)\, \boldsymbol{g}(1,2)\, \psi_\mathrm{A}(1)\, \psi_\mathrm{B}(2)\, d\tau_2 d\tau_1 \\ K(\mathrm{A, B}) &= \langle \mathrm{A, B}|\boldsymbol{g}|\mathrm{B, A}\rangle = \iint \psi_\mathrm{A}^*(1)\, \psi_\mathrm{B}^*(2)\, \boldsymbol{g}(1,2)\, \psi_\mathrm{B}(1)\, \psi_\mathrm{A}(2)\, d\tau_2 d\tau_1 \end{aligned} \tag{13}$$

The exchange interaction function $\boldsymbol{g}$ of electron 1 (with A set) and 2 (with B set of quantum numbers) which is part of Hamiltonian (1), is usually decomposed into the electric term $\left(\frac{1}{r_{12}}\right)$, most significant in calculations, and into the Breit term $B(1, 2)$ about a thousand times less significant:

$$\boldsymbol{g}(1,2) = \frac{1}{r_{12}} + B(1,2) \tag{14}$$

The Breit term is usually decomposed into two terms – the magnetic term $g^\mathrm{M}(1, 2)$ and retardation term $g^\mathrm{R}(1, 2)$ (where $g^\mathrm{M} \approx 10 g^\mathrm{R}$).

$$\begin{aligned} B(1,2) &= \{g^\mathrm{M}(1,2)\} + \{g^\mathrm{R}(1,2)\} \\ &= \left\{ -\frac{\vec{\alpha}(1)\, \vec{\alpha}(2)}{r_{12}} \right\} + \left\{ \frac{1}{2} \frac{\vec{\alpha}(1)\, \vec{\alpha}(2)}{r_{12}} - \frac{1}{2} \left[\frac{\vec{\alpha}(1) \vec{r}_{1,2}\, \vec{\alpha}(2) \vec{r}_{1,2}}{r_{12}^3} \right] \right\} \end{aligned} \tag{15}$$

The matrix elements $J(\mathrm{A, B})$ and $K(\mathrm{A, B})$ obtained from (10) were simplified by Grant [10] using Racah algebra, and in [10, 22, 18] solved separately for all three interactions. Finally, the expression for total energy E of the atom consisting of closed shells of electrons was found:

$$E = E^\mathrm{O} + E^\mathrm{C} + E^\mathrm{M} + E^\mathrm{R}. \tag{16}$$

In (16) terms are defined as:

$$E^\mathrm{O} = \sum_\mathrm{A} q_\mathrm{A} I(\mathrm{A}) = \text{single particle contribution} \tag{17}$$

and E^C = contribution of the Coulomb repulsion, E^M = magnetic energy, E^R = retardation energy. The explicit form of E^C is:

$$\begin{aligned} E^\mathrm{C} = \sum_\mathrm{A} \Bigg\{ \frac{1}{2} q_\mathrm{A}(q_\mathrm{A} - 1)\, F_\mathrm{C}^0(\mathrm{A, A}) - \frac{q_\mathrm{A}}{4} \sum_{\nu > 0} q_\mathrm{A} \Gamma_{j_\mathrm{A} \nu j_\mathrm{A}}\, F_\mathrm{C}^\nu(\mathrm{A, A}) \Bigg\} \\ + \frac{1}{2} \sum_{\mathrm{B} \neq \mathrm{A}} q_\mathrm{A} q_\mathrm{B} \left[F_\mathrm{C}^0(\mathrm{A, B}) - \sum_\nu \frac{1}{2} \Gamma_{j_\mathrm{A} \nu j_\mathrm{B}}\, G_\mathrm{C}^\nu(\mathrm{A, B}) \right] \Bigg\} \end{aligned} \tag{18}$$

with coefficients $\Gamma_{j_A \nu j_B}$ defined by Grant [10] and with exact validity only for closed shells. Here q_A and q_B are the numbers of electrons on closed shells A and B and F_C^ν and G_C^ν are Slater integrals for Coulomb interaction:

$$R_C^\nu(A, B, C, D) = \int_0^\infty [P_A P_B + Q_A Q_B] \frac{1}{r} Y_C^\nu(C, D; r) dr \tag{19}$$

and

$$\begin{aligned} G_C^\nu(A, B) &= R_C^\nu(A, B, A, B) \\ F_C^\nu(A, B) &= R_C^\nu(A, A, B, B) . \end{aligned} \tag{20}$$

The potential function $Y_C^\nu(C, D; r)$ is defined in Eq. (26). Magnetic and retardation energy E^M and E^R, derived from the term of Breit interaction (15), are also defined in [12] and [18]; in form they are rather similar to (18), with more complicated coefficients. Because they are generally small, we neglected them in our calculations. They can be introduced as perturbation correction in more exact approximation. From Eq. (18), using the variation principle which minimizes the total energy E, the final set of relativistic Eqs. (21) and (22) was found in [10], defining the orthonormal radial functions $P_A(r)$, $Q_A(r)$ for each electron with the set of quantum numbers A (i.e. with n_A, k_A, a_A):

$$\begin{aligned} &\frac{dP_A}{dr} + \frac{k_A}{r} P_A + \left[2c + \frac{1}{rc} Y^E(A; r) - \frac{\varepsilon_{AA}}{c}\right] Q_A \\ &\qquad = W_Q(A; r) + \sum_{B \neq A} \frac{1}{c} \varepsilon_{AB} \delta(j_A, j_B) \delta(a_A, a_B) Q_B , \end{aligned} \tag{21}$$

$$\begin{aligned} &\frac{dQ_A}{dr} - \frac{k_A}{r} Q_A - \frac{1}{c}\left[\frac{1}{r} Y^E(A; r) - \varepsilon_{AA}\right] P_A \\ &\qquad = -W_P(A; r) - \sum_{B \neq A} \frac{1}{c} \varepsilon_{AB} \delta(j_A, j_B) \delta(a_A, a_B) P_B . \end{aligned} \tag{22}$$

The potential functions are defined:

$$Y^E(A; r) = r V(r) - \sum_A q_A Y_C^0(A, A; r) + \sum_\nu \frac{1}{2} q_A \Gamma_{j_A \nu j_A} Y_C^\nu(A, A; r) \tag{23}$$

$$W_P(A; r) = -\frac{1}{rc} \sum_{B \neq A} \sum_\nu \frac{1}{2} q_B Y_C^\nu(A, B; r) P_B(r) \Gamma_{j_A \nu j_B} \tag{24}$$

$$W_Q(A; r) = -\frac{1}{rc} \sum_{B \neq A} \sum_\nu \frac{1}{2} q_B Y_C^\nu(A, B; r) Q_B(r) \Gamma_{j_A \nu j_B} \tag{25}$$

Here $V(r)$ is the nuclear potential, which we approximate as $\frac{Z}{r}$ (point nucleus). The basic potential functions $Y_C^\nu(A, B; r)$ are defined as the integral:

$$Y_C^\nu(A, B; r) = r \int_0^\infty U_\nu(r, S) [P_A(S) P_B(S) + Q_A(S) Q_B(S)] dS \tag{26}$$

where

$$U_\nu(r,S) = r^\nu/S^{\nu+1} \quad \text{if} \quad r<S$$
$$= S^\nu/r^{\nu+1} \quad \text{if} \quad r>S\,.$$

We used the original Eq. (18), (21) and (22) derived by Grant [10] for atoms with closed shells also for calculation of atoms with nonclosed shells. As correction here for open shells, we generally used the actual number of electrons present in the open shell as q_A or q_B; for closed shells, q_A in Eqs. (18), (23), (24), (25) is equal to $(2j_A+1)$ (number of electron in full shell A) as derived by Grant [10]. This is the correction used by Hartree [23] (pgs. 110, 112) in the non-relativistic case. For both closed and open shells we used common coefficients $\Gamma_{j_A\nu j_B}$, which are exactly valid only for closed shells. However, in each atom only a few (1 or 2) open shells of valence electrons were present which were calculated with non-exact $\Gamma_{j_A\nu j_B}$ coefficients and a great majority of inner shells were calculated correctly. Therefore, we hope, our results are not substantially affected by this approximation.

Slater [24] suggested another approximative method for calculating the average energy (weighted mean energy) of an atom containing few open shells in NRHF calculations. This method again uses the coefficients (of $\Gamma_{j_A\nu j_B}$ type) which are exactly valid only for closed shells. In the relativistic cases Slater's method leads to replacing coefficient $q_A\Gamma_{j_A\nu j_A}$ in the second term of equation (18) and in the third term of equation (23):

$$q_A\Gamma_{j_A\nu j_A} \xrightarrow{\text{replaced by}} (q_A-1)\frac{(2j_A+1)}{2j_A}\Gamma_{j_A\nu j_A} \tag{27}$$

with q_A = number of electrons in open shell A. Such replacement slightly changes wave functions and total energy E^C, which is then called average energy E^C_{AV}. This approach was recently used by Mann and Waber [19] and we also calculated average energies E^C_{AV} using replacement (27) in (18).

For shells with (nlj) quantum numbers, to describe our results we use the notation: 1, 2, 3 ... for main quantum number n, the usual letter s, p, d, f, g ..., for $l = 0, 1, 2, 3, 4$ etc ... and numbers 1/2, 3/2, 5/2, 7/2, 9/2 etc for $j = l + \frac{1}{2}$ or $l - \frac{1}{2}$. For brevity in some tables we use the notation n, l, a when n, l is as described above and a = signum of spin number which defines $j = l + \frac{1}{2}a$ (e.g. $5f_{5/2} = 5f-$, $5f_{7/2} = 5f+$, see also Table 1).

2.2. Computer Program and Calculations

In our calculations we use the computer program of Coulthard [25] which was adapted for calculation of large atoms. This program which was originally written for point nucleus in FORTRAN IV language for IBM computer 7044, maximally allowed calculations of atoms with 24 shells (Rn) and used 180 tabulation points for variable t $\left(\text{where radius } r = \frac{e^t}{1370} \text{ is in Bohr units}\right)$ going up from $t = -3/16$ with step 1/16. We extend this program to a maximum of 46 shells, using 90 tabulation points with step 1/8 going up from $t = -3/8$ (further referred to as 46 × 90 program). This allowed us to calculate all heavy atoms up to $Z = 130$ almost using the full memory of IBM–7044. We adjusted the program further for FORTRAN V language and used the UNIVAC 1108 computer of the Université de Paris XI, Orsay. This computer has a substantially bigger memory than IBM–7044, so we also used here the 180 point tabulation set for atoms with up to 46 shells and original step 1/16 of t starting from $t = -3/16$ (further referred to as 46 × 180 program). The results of calculations with 46 × 90 program are practically identical to those with 46 × 180 program, as seen in Table 1 for the case of Hg. We also corrected some coefficients $\Gamma_{j_A \nu j_B}$ in the original Coulthard program which were incorrectly derived in [10] and were later corrected [11]. For acceleration of all calculations we used the previously calculated wave function of neighbour elements of close configuration as starting values for calculation of the next (relative) configuration. In Table 1 Coulthard results [14] are presented and compared with ours using corrected coefficients $\Gamma_{j_A \nu j_B}$. The differences are visible in the $5f$ shell, due to the corrected coefficients in our program (see 46 × 180 program). From Table 1 we see that the results of both our programs are the same for eigenvalues and differ only slightly in total energy. The results in Table 1 are compared with Mann and Johnson [18] for Hg (calculated by SCF Dirac-Fock program with finite nucleus approximation) and with [27] experimental values. One can see that our eigenvalues are almost the same as in [18], with the exclusion of $1s+$ electron, wich is closer tot the experimental value in the case of finite nucleus approximation [18]. This change also diminishes somewhat the total energy of [18]. For more heavy elements this effect became more important – e.g. for 114 and 126 elements in DFS approximation it was found that the eigenvalue of $1s+$ electron is changed $\sim 1\%$ and 3.5% respectively [26], with practically no effect on shells with $n > 2$. We also calculated some configurations of 126 element with our program and compared our eigenvalues with eigenvalues of Mann and Waber [19] calculated with finite nuclear approximation for 126 element in (118) $5g^2 6f^2 8s^2 8p^2$ configuration. The results were similar to those in [26]; our eigenvalues for $1s+$ and $2s+$ of 126 were about 3.5% higher than the more correct values of Mann and Waber. All of our other eigenvalues were close to the eigenvalues of [19].

For this reason we limited our calculations (using point nucleus approximation) maximally to 120 element, where the difference of our $1s+$ and $2s+$ value will be $\sim 1.5\%$ of values calculated as in [19].

However, a majority of chemical and spectroscopic results can be obtained from ionization potentials of outer shells, which our program calculates correctly up to $Z = 120$.

Finally, for simplification in our program, we neglect all magnetic and retardation terms in Eq. (16). These terms are relatively small, but absolutely not negligible as shown in [19] and [18]. Generally, they shift all calculated total energies of all close configurations in one way by some practically constant value. The magnetic terms substract about 0.1% from calculated total energy and the retardation terms add about 0.01% to this energy. These terms can be calculated in good approximation as perturbation of total energy, using the wave functions calculated only from Coulomb terms. We believe that the conclusions concerning ionization potentials, of transition energy between energy levels (X-rays) and of atomic or ionic radii, are not substantially affected by neglecting magnetic and retardation terms.

Table 1. Comparison of eigenvalues and total energies (-values in Ry) calculated for Hg^{80}

Subshell	j	No. of electrons	DHF This work "46 × 90" program	DHF This work "46 × 180" program	Energy DHF Coulthard [14] "25 × 180" program	DHF Finite nucleus [18]	DFS[a] Point nucleus [7] 2/3 of Slater potential	Experimental X rays energy levels [27]
$1s+$	1/2	2	6152.2798	6152.2898	6152.30	6148.6546	6152.52	6108.38 ± 0.06
$2s+$	1/2	2	1101.0642	1101.0698	1101.07	1100.5287	1101.36	1091.02 ± 0.07
$2p-$	1/2	2	1053.7087	1053.7126	1053.72	1053.7019	1054.02	1044.68 ± 0.05
$2p+$	3/2	4	910.2631	910.2805	910.28	910.3115	910.60	903.20 ± 0.03
$3s+$	1/2	2	266.3593	266.3511	266.35	266.2319	266.68	262.12 ± 0.08
$3p-$	1/2	2	245.2829	245.2732	245.28	245.2758	245.62	241.30 ± 0.09
$3p+$	3/2	2	213.0669	213.0753	213.08	213.0895	213.42	209.60 ± 0.03
$3d-$	3/2	4	178.8525	178.8590	178.86	178.8730	179.20	175.62 ± 0.02
$3d+$	5/2	6	172.0121	172.0257	172.03	172.0400	172.38	169.00 ± 0.02
$4s+$	1/2	2	61.3402	61.3269	61.33	61.2979	61.64	59.16 ± 0.07
$4p-$	1/2	2	52.2594	52.2456	52.25	52.2476	52.56	50.08 ± 0.17
$4p+$	3/2	4	44.3730	44.3719	44.37	44.3769	44.68	42.30 ± 0.10
$4d-$	3/2	4	29.5907	29.5886	29.59	29.5933	29.90	28.14 ± 0.07
$4d+$	5/2	6	28.0947	28.1000	28.10	28.1050	28.42	26.76 ± 0.09
$4f-$	5/2	6	8.9288	8.9308	8.937	8.9458	9.254	7.86 ± 0.04
$4f+$	7/2	8	8.6050	8.6083	8.615	8.6234	8.930	7.58 ± 0.04
$5s+$	1/2	2	10.2176	10.2125	10.212	10.2064	10.450	9.18 ± 0.09
$5p-$	1/2	2	7.0804	7.0756	7.076	7.0757	7.296	6.24 ± 0.09
$5p+$	3/2	4	5.6836	5.6831	5.683	5.6839	5.884	4.56 ± 0.09
$5d-$	3/2	4	1.3002	1.2996	1.300	1.3001	1.446	1.228 ± 0.10
$5d+$	5/2	6	1.1476	1.1487	1.149	1.1493	1.288	1.090 ± 0.10
$6s+$	1/2	2	0.6573	0.6566	0.6566	0.6561	0.178	0.768 ± 0.10
E_{total}:			39307.740	39307.362	39307.4	39298.167	39306.62	

[a] In this column are quoted binding energies (not eigenvalues) from [7].

3. Results

In our self-consistent calculations we calculate the set of eigenvalues ε_{AA} for each element by solving Eq. (21) and (22) for each subshell (in which we omit all nondiagonal terms containing ε_{AB}, as negligible) with error 10^{-7} allowed for its integration procedure. We also obtained the sets of potentials $Y^E(A; r)$ and radial wave functions P_A, Q_A with error 10^{-5} allowed for their iteration or integration procedures, respectively.

After obtaining the convergency of these values, we usually formed the total energies as follows:

TE = TOTAL ENERGY = $E^O + E^C$ as defined in (17) and (18).

AE = AVERAGE ENERGY = $E^O + E^C_{AV}$, with E^O defined in (17) and (18) but using replacement (27) in Eq. (18) for E^C_{AV} calculations.

Both TE and AE values used wave functions P_A, Q_A which were obtained without replacement (27) in Eq. (23) but used the actual number of electrons present, q_A, for each open shell. This we will call wave functions „Hartree type". Results for a few atoms and ions with these functions are presented in the first three columns of Table 2.

In our computer program we also have other possible variants for calculations of wave functions P_A, Q_A – using (21) and (22) (omitting terms containing ε_{AB}) where the replacement of (27) is used in Eq. (23) during self-consistent calculations. We call the wave functions obtained in this way "Slater type". Using this "Slater type" wave function, we again calculated total energies:

TE_S = TOTAL ENERGY (SLATER) = $E^O + E^C$ as described in (17) and (18).

AE_S = AVERAGE ENERGY (SLATER) = $E^O + E^C_{AV}$ with replacement (27) in (18).

The results from "Slater type" wave functions are presented in the last three columns of Table 2. In comparison to results in Table 2 for TE, AE or TE_S, AE_S, one can see that both types of wave functions give absolutely somewhat different total energies and average energies – with AE, AE_S lying lower than TE, TE_S. However, the shift from TE, TE_S to AE, AE_S (expressed as their difference, Δ) is the same, within the errors of calculations, for both wave functions (either "Slater" or "Hartree" type). In most of our results we use the "Hartree type" wave functions, with TE and AE. To determine ground state it is important to use the correct energetic difference between the close-lying configurations – not the absolute value of TE or AE (which is affected much more by point nucleus approximation than by use of the "Slater type" wave function, see e.g. cases Sm, Yb in Table 3). In Table 3 we compare our results with other available results, throughout the periodic system. Our results (with 46 × 90 program, using point nucleus approximation) are in good accord with the results of Mann and Johnson [18] (using finite nucleus approximation). Results up to Ne are identical with [18], then start to differ slightly up to Kr, with a growing difference up to 120 element, due to our point nucleus approximation (less exact than [18]).

On the other hand, the results of [17] (which should use the same formulae as we do, i.e. also with point nucleus approximation) differ from ours substantially more than do the results of [18]. They are considerably higher than our results (giving smaller $-E_{\text{Total}}$) or those of [18] which are certainly more correct. In the

Table 2

Element	Z	Configuration	Wave function "Hartree type"			Wave function "Slater type"		
			$-$TE(AU)	$-$AE(AU)	Δ	$-$TE$_S$(AU)	$-$AE$_S$(AU)	Δ
Eu	63	(Xe) $4f_-^5\ 4f_+^2\ 6s_+^2$	10847.4429	10847.4708	0.0279	10847.3898	10847.4177	0.0279
Eu	63	(Xe) $4f_-^6\ 5d_-^1\ 6s_+^2$	10847.6021	10847.6064	0.0045	10847.5961	10847.6005	0.0044
Gd^{1+}	64	(Xe) $4f_-^6\ 4f_+^1\ 5d_-^1\ 6s_+^1$	11275.2048	11275.2203	0.0154	11275.1719	11275.1873	0.0154
Dy^{1+}	66	(Xe) $4f_-^6\ 4f_+^3\ 6s_+^2$	12162.6265	12162.6510	0.0245	12162.5811	12162.6053	0.0244
Nd^{2+}	60	(Xe) $4f_-^4$	9625.3037	9625.3201	0.0164	9625.2782	9625.2946	0.0164

Table 3. Comparison of calculated total energies (-values in Ry)

Element	Z	E_{DHF} this work	E_{DHF} [18]	E_{DHF} [17]	E_{DFS} 2/3 Slater potential [7]	E_{DFS} [5]	E_{NRHF} [2]
He	2	5.7236	5.7236	5.72349		5.5991	4.3430
Be	4	29.1518	29.1518			28.4645	29.1903
Ne	10	257.3840	257.3838	257.3486	257.262	255.1814	256.9663
Na	11	324.1566		324.1065	324.112	321.5484	323.5997
Ar	18	1057.3708	1057.3673	1057.082	1057.274	1052.532	1053.4645
Zn	30	3589.2554	3589.2244		3589.136	2580.873	3554.8922
Br	35	5210.1294		5207.233	5209.950	5199.642	5144.0685
Kr	36	5577.7922	5557.7193		5577.614	5566.928	5503.2799
Cd	48	11186.9604	11186.6381			11171.96	10928.9957
Xe	54	14894.4372	14893.7970		14894.08	14877.31	14463.0543
Sm	62	20860.2604	20858.7635			20841.25	20067.4636
Yb	70	28138.7230	28135.4602			28118.75	26779.6008
W	74	32317.728	32312.6826		32316.94	32296.11	30571.2385
Hg	80	39307.740	39298.1672		39306.62	39284.19	36813.8350
Pb	82	41839.818	41828.9999			41815.68	39043.7729
Rn	86	47223.034	47204.9084	47156.46	47221.56	47197.93	43729.1919
Pu	94	59357.676	59315.6687		59284.249 [9]	59332.09	54011.8213
Md	101	71680.354			71552.261 [9]	71655.21	64055.4546
No	102	73586.764	73486.7522		73443.480 [9]		65572.3604
118	118	110320.646	109635.2509 [19]		109503.757 [9]	109402.64 [8]	92641.013
120	120	115963.612	115073.1418 [19]		114912.660 [9]	114796.48 [8]	96395.031

case of Rn [17] gives the total energy 48.46 Ry higher than in [18] but [17] should yield only lower value because of point nucleus approximation (e.g. – 18.126 Ry lower, as in our results in comparison to [18]). This discrepancy probably indicates that the definition of total energy in [17] differs from the definition derived by Grant [10] used in [18] and in our program.

Further results presented in Table 3 for comparison were obtained by DFS and point nucleus approximation using the full Slater exchange potential with factor 1 (see [5]) or using the Slater exchange potential with factor 2/3 (see [7]) or for some heavy atoms, the DFS results are compared with finite nucleus and full Slater potential (see [8]) or 2/3 of Slater potential (see [9]). The DFS results with 2/3 Slater potential and point nucleus are very close to ours [7]. The results for finite nucleus and heavy atoms (118, 120) in [8, 9] are higher than correct values of [18], when our results in this region are lower than [18]. The results of NRHF [2] for all more heavy atoms are generally incorrect; they are not too far from our values (and from experimental values, see last columns of Table 3) for elements below Ar, but for elements with $Z > 20$ they differ substantially with unrealistic differences for all heavy elements above $Z > 50$. In Table 4 (for all elements from H to Ca systematically) experimental values of total energies are presented – calculated as the sum of ionization potentials of all electrons from each element – which is known [28] up to Ca ($Z = 20$). The date [28] are given in eV. They were recalculated to AU with constant: $1\,\mathrm{AU} = 2\,\mathrm{Ry} = 27.196\,\mathrm{eV}$. Experimental total energies are compared in Table 4 with our TE and AE. The agreement of calculated values with experimental ones is good (when AE are somewhat closer than TE to experimental values). The main results of this work are collected in

Table 4. Comparison of calculated and experimental total energies

Element	Z	Experimental [28]	E_{total}(AU)	
			This work –TE	This work –AE
H	1	0.5000	0.500007	0.500007
He	2	2.9049	2.8618	2.8618
Li	3	7.4824	7.4335	7.4335
Be	4	14.6764	14.5759	14.5759
B	5	24.6715	24.5366	24.5366
C	6	37.8762	37.6574	37.6574
N	7	54.6414	54.3243	54.3316
O	8	75.1506	74.8326	74.8439
F	9	99.8600	99.5119	99.5215
Ne	10	129.1200	128.6920	128.6920
Na	11	162.5160	162.0783	162.0783
Mg	12	200.4177	199.9353	199.9353
Al	13	242.8432	242.3315	242.3315
Si	14	290.0247	289.4503	289.4503
P	15	342.1316	341.4945	341.4993
S	16	398.9083	398.6052	342.6125
Cl	17	461.6284	460.9471	460.9533
Ar	18	529.3982	528.6854	528.6854
K	19	602.2928	601.5280	601.5280
Ca	20	680.4720	679.7128	679.7128

Table 5. Total energies in the periodic system

Symbol	Z	Electron structure	DHF calculated		Ground state
			$-$TE(AU)	$-$AE(AU)	[28], c) [2], d) [9]
H	1	$1s_{+}^{1}$	$\underline{0.500007}$	$\underline{0.500007}$	$1s^1$ c)
		$2s_{+}^{1}$	0.125004	0.125004	
He	2	$1s_{+}^{2}$	$\underline{2.8618}$	$\underline{2.8618}$	$1s^2$ c)
		$1s_{+}^{1}$ $2s_{+}^{1}$	2.1663	2.1663	
Li	3	(He) $2s_{+}^{1}$	$\underline{7.4335}$	$\underline{7.4335}$	(He) $2s^1$
Be	4	(He) $2s_{+}^{2}$	$\underline{14.5759}$	$\underline{14.5759}$	(He) $2s^2$
B	5	(He) $2s_{+}^{2}$ $2p_{-}^{1}$	$\underline{24.5366}$	$\underline{24.5366}$	(He) $2s^2\,2p^1$
		(He) $2s_{+}^{1}$ $2p_{-}^{2}$	24.3266	24.3266	
C	6	(He) $2s_{+}^{2}$ $2p_{-}^{2}$	$\underline{37.6574}$	$\underline{37.6574}$	(He) $2s^2\,2p^2$ c)
		(He) $2s_{+}^{1}$ $2p_{-}^{2}$ $2p_{+}^{1}$	37.3501	37.3561	
N	7	(He) $2s_{+}^{2}$ $2p_{-}^{2}$ $2p_{+}^{1}$	$\underline{54.3243}$	$\underline{54.3316}$	(He) $2s^2\,2p^3$
		(He) $2s_{+}^{1}$ $2p_{-}^{2}$ $2p_{+}^{2}$	53.8542	53.8637	
O	8	(He) $2s_{+}^{2}$ $2p_{-}^{2}$ $2p_{+}^{2}$	$\underline{74.8326}$	$\underline{74.8439}$	(He) $2s^2\,2p^4$
		(He) $2s_{+}^{1}$ $2p_{-}^{2}$ $2p_{+}^{3}$	74.1678	74.1761	
F	9	(He) $2s_{+}^{2}$ $2p_{-}^{2}$ $2p_{+}^{3}$	$\underline{99.5119}$	$\underline{99.5215}$	(He) $2s^2\,2p^5$
		(He) $2s_{+}^{2}$ $2p_{-}^{2}$ $2p_{+}^{2}$ $3s_{+}^{1}$	99.0463	99.0606	
		(He) $2s_{+}^{1}$ $2p_{-}^{2}$ $2p_{+}^{4}$	98.6201	98.6201	
Ne	10	(He) $2s_{+}^{2}$ $2p_{-}^{2}$ $2p_{+}^{4}$	$\underline{128.6920}$	$\underline{128.6920}$	(He) $2s^2\,2p^6$
		(He) $2s_{+}^{2}$ $2p_{-}^{2}$ $2p_{+}^{3}$ $3s_{+}^{1}$	128.1496	128.1615	
Na	11	(Ne) $3s_{+}^{1}$	$\underline{162.0783}$	$\underline{162.0783}$	(Ne) $3s^1$
Mg	12	(Ne) $3s_{+}^{2}$	$\underline{199.9353}$	$\underline{199.9353}$	(Ne) $3s^2$
		(Ne) $3s_{+}^{1}$ $3p_{-}^{1}$	199.8420	199.8420	
Al	13	(Ne) $3s_{+}^{2}$ $3p_{-}^{1}$	$\underline{242.3315}$	$\underline{242.3315}$	(Ne) $3s^2\,3p^1$
		(Ne) $3s_{+}^{1}$ $3p_{-}^{2}$	242.1512	242.1512	
Si	14	(Ne) $3s_{+}^{2}$ $3p_{-}^{2}$	$\underline{289.4503}$	$\underline{289.4503}$	(Ne) $3s^2\,3p^2$
		(Ne) $3s_{+}^{1}$ $3p_{-}^{2}$ $3p_{+}^{1}$	289.2049	289.2091	

Table 5 (continued)

Symbol	Z	Electron structure	DHF calculated		Ground state
			$-$TE(AU)	$-$AE(AU)	[28], c) [2], d) [9]
P	15	(Ne) $3s_+^2$ $3p_-^2$ $3p_+^1$	$\underline{341.4945}$	$\underline{341.4993}$	(Ne) $3s^2\,3p^3$
		(Ne) $3s_+^1$ $3p_-^2$ $3p_+^2$	341.1494	341.1559	
S	16	(Ne) $3s_+^2$ $3p_-^2$ $3p_+^2$	$\underline{398.6052}$	$\underline{398.6125}$	(Ne) $3s^2\,3p^4$
		(Ne) $3s_+^1$ $3p_-^2$ $3p_+^3$	398.1488	398.1543	
Cl	17	(Ne) $3s_+^2$ $3p_-^2$ $3p_+^3$	$\underline{460.9471}$	$\underline{460.9533}$	(Ne) $3s^2\,3p^5$
		(Ne) $3s_+^2$ $3p_-^2$ $3p_+^2$ $4s_+^1$	460.6172	460.6260	
		(Ne) $3s_+^1$ $3p_-^2$ $3p_+^4$	460.3677	460.3677	
Ar	18	(Ne) $3s_+^2$ $3p_-^2$ $3p_+^4$	$\underline{528.6854}$	$\underline{528.6854}$	(Ne) $3s^2\,3p^6$
		(Ne) $3s_+^2$ $3p_-^2$ $3p_+^3$ $4s_+^1$	528.2937	528.3010	
K	19	(Ar) $4s_+^1$	$\underline{601.5280}$	$\underline{601.5280}$	(Ar) $4s^1$
Ca	20	(Ar) $4s_+^2$	$\underline{679.7128}$	$\underline{679.7128}$	(Ar) $4s^2$
		(Ar) $4s_+^1$ $4p_-^1$	679.6527	679.6527	
Sc	21	(Ar) $3d_-^1$ $4s_+^2$	$\underline{763.3895}$	$\underline{763.3959}$	(Ar) $3d^1\,4s^2$
		(Ar) $3d_-^2$ $4s_+^1$	763.3150	763.3216	
		(Ar) $4s_+^2$ $4p_-^1$	763.2853	763.2853	
		(Ar) $4s_+^1$ $4p_-^2$	763.1676	763.1676	
Ti	22	(Ar) $3d_-^2$ $4s_+^2$	$\underline{852.8392}$	$\underline{852.8487}$	(Ar) $3d^2\,4s^2$ c)
		(Ar) $3d_-^3$ $4s_+^1$	852.7797	852.7856	
V	23	(Ar) $3d_-^3$ $4s_+^2$	$\underline{948.2191}$	$\underline{948.2269}$	(Ar) $3d^3\,4s^2$
		(Ar) $3d_-^4$ $4s_+^1$	948.1693	948.1693	
		(Ar) $3d_-^4$ $3d_+^1$	948.0205	948.0255	
Cr	24	(Ar) $3d_-^4$ $4s_+^2$	$\underline{1049.6820}$	$\underline{1049.6820}$	c)
		(Ar) $3d_-^4$ $3d_+^1$ $4s_+^1$	1049.6319	1049.6389	(Ar) $3d^5\,4s^2$
		(Ar) $3d_-^4$ $3d_+^2$	1049.2778	1049.2811	
Mn	25	(Ar) $3d_-^4$ $3d_+^1$ $4s_+^2$	$\underline{1157.3673}$	$\underline{1157.3761}$	(Ar) $3d^5\,4s^2$ c)
		(Ar) $3d_-^4$ $3d_+^2$ $4s_+^1$	1157.3251	1157.3375	
		(Ar) $3d_-^4$ $3d_+^3$	1157.1672	1157.1791	

Table 5 (continued)

Symbol	Z	Electron structure	DHF calculated		Ground state
			−TE(AU)	−AE(AU)	[28], c) [2], d) [9]
Fe	26	(Ar) $3d_-^4\ 3d_+^2\ 4s_+^2$	$\underline{1271.4370}$	$\underline{1271.4518}$	(Ar) $3d^6\ 4s^2$ c)
		(Ar) $3d_-^4\ 3d_+^3\ 4s_+^1$	1271.4017	1271.4168	
		(Ar) $3d_-^4\ 3d_+^4$	1271.2402	1271.2518	
Co	27	(Ar) $3d_-^4\ 3d_+^3\ 4s_+^2$	$\underline{1392.0441}$	$\underline{1392.0620}$	(Ar) $3d^7\ 4s^2$ c)
		(Ar) $3d_-^4\ 3d_+^4\ 4s_+^1$	1392.0155	1392.0299	
		(Ar) $3d_-^4\ 3d_+^5$	1391.8492	1391.8571	
Ni	28	(Ar) $3d_-^4\ 3d_+^4\ 4s_+^2$	$\underline{1519.3420}$	$\underline{1519.3588}$	(Ar) $3d^8\ 4s^2$ c)
		(Ar) $3d_-^4\ 3d_+^5\ 4s_+^1$	1519.3194	1519.3290	
		(Ar) $3d_-^4\ 3d_+^6$	1519.1485	1519.1485	
Cu	29	(Ar) $3d_-^4\ 3d_+^5\ 4s_+^2$	$\underline{1653.4852}$	$\underline{1653.4962}$	
		(Ar) $3d_-^4\ 3d_+^6\ 4s_+^1$	1653.4679	1653.4679	(Ar) $3d^{10}\ 4s^1$ c)
		(Ar) $3d_-^4\ 3d_+^6\ 4p_-^1$	1653.3510	1653.3510	
Zn	30	(Ar) $3d_-^4\ 3d_+^6\ 4s_+^2$	$\underline{1794.6277}$	$\underline{1794.6277}$	(Ar) $3d^{10}\ 4s^2$
		(Ar) $3d_-^4\ 3d_+^6\ 4s_+^1\ 4p_-^1$	1794.4993	1794.4993	
		(Ar) $3d_-^4\ 3d_+^5\ 4s_+^2\ 4p_-^1$	1794.3076	1794.3200	
Ga	31	$(3d^{10})\ 4s_+^2\ 4p_-^1$	$\underline{1942.5833}$	$\underline{1942.5833}$	(Zn) $4p^1$
		$(3d^{10})\ 4s_+^1\ 4p_-^2$	1942.3701	1942.3701	
Ge	32	$(3d^{10})\ 4s_+^2\ 4p_-^2$	$\underline{2097.4862}$	$\underline{2097.4862}$	(Zn) $4p^2$
		$(3d^{10})\ 4s_+^1\ 4p_-^2\ 4p_+^1$	2097.2097	2097.2138	
As	33	$(3d^{10})\ 4s_+^2\ 4p_-^2\ 4p_+^1$	$\underline{2259.4721}$	$\underline{2259.4767}$	(Zn) $4p^3$
		$(3d^{10})\ 4s_+^1\ 4p_-^2\ 4p_+^2$	2259.1053	2259.1115	
Se	34	$(3d^{10})\ 4s_+^2\ 4p_-^2\ 4p_+^2$	$\underline{2428.6280}$	$\underline{2428.6348}$	(Zn) $4p^4$
		$(3d^{10})\ 4s_+^1\ 4p_-^2\ 4p_+^3$	2428.1646	2428.1697	
Br	35	$(3d^{10})\ 4s_+^2\ 4p_-^2\ 4p_+^3$	$\underline{2605.0647}$	$\underline{2605.0702}$	(Zn) $4p^5$
		$(3d^{10})\ 4s_+^2\ 4p_-^2\ 4p_+^3\ 5s_+^1$	2604.7769	2604.7848	
		$(3d^{10})\ 4s_+^1\ 4p_-^2\ 4p_+^4$	2604.4978	2604.4978	

Table 5 (continued)

Symbol	Z	Electron structure	DHF calculated −TE(AU)	DHF calculated −AE(AU)	Ground state [28], c) [2] d) [9]
Kr	36	$(3d^{10})$ $4s_+^2$ $4p_-^2$ $4p_+^4$	$\underline{2788.8961}$	$\underline{2788.8961}$	(Zn) $4p^6$
		$(3d^{10})$ $4s_+^2$ $4p_-^2$ $4p_+^3$ $5s_+^1$	2788.5589	2788.5653	
Rb	37	(Kr) $5s_+^1$	$\underline{2979.8453}$	$\underline{2979.8453}$	(Kr) $5s^1$ c)
		(Kr) $4d_-^1$	2979.7308	2979.7338	
Sr	38	(Kr) $5s_+^2$	$\underline{3178.1267}$	$\underline{3178.1267}$	(Kr) $5s^2$ c)
		(Kr) $5s_+^1$ $5p_-^1$	3178.0724	3178.0724	
		(Kr) $4d_-^1$ $5s_+^1$	3178.0528	3178.0555	
Y	39	(Kr) $4d_-^1$ $5s_+^2$	$\underline{3383.8205}$	$\underline{3383.8250}$	(Kr) $4d^1$ $5s^2$ c)
		(Kr) $5s_+^2$ $5p_-^1$	3383.7748	3383.7748	
		(Kr) $4d_-^2$ $5s_+^1$	3383.7626	3383.7678	
		(Kr) $5s_+^1$ $5p_+^2$	3383.6682	3383.6682	
Zr	40	(Kr) $4d_-^2$ $5s_+^2$	$\underline{3597.1583}$	$\underline{3597.1652}$	(Kr) $4d^2$ $5s^2$ c)
		(Kr) $4d_-^3$ $5s_+^1$	3597.1198	3597.1244	
Nb	41	(Kr) $4d_-^3$ $5s_+^2$	$\underline{3818.2628}$	$\underline{3818.2685}$	c)
		(Kr) $4d_-^4$ $5s_+^1$	3818.2470	3818.2470	(Kr) $4d^4$ $5s^1$
Mo	42	(Kr) $4d_-^4$ $5s_+^2$	$\underline{4047.2551}$	4047.2551	c)
		(Kr) $4d_-^4$ $4d_+^1$ $5s_+^1$	4047.2517	$\underline{4047.2572}$	(Kr) $4d^5$ $5s^1$
		(Kr) $4d_-^4$ $4d_+^2$	4047.1823	4047.1903	
Tc	43	(Kr) $4d_-^4$ $4d_+^2$ $5s_+^1$	$\underline{4284.2622}$	$\underline{4284.2718}$	c)
		(Kr) $4d_-^4$ $4d_+^1$ $5s_+^2$	4284.2423	4284.2488	(Kr) $4d^5$ $5s^2$
		(Kr) $4d_-^4$ $4d_+^3$	4284.2075	4284.2174	
Ru	44	(Kr) $4d_-^4$ $4d_+^3$ $5s_+^1$	$\underline{4529.3901}$	$\underline{4529.4017}$	(Kr) $4d^7$ $5s^1$ c)
		(Kr) $4d_-^4$ $4d_+^4$	4529.3587	4529.3683	
		(Kr) $4d_-^4$ $4d_+^2$ $5s_+^2$	4529.3535	4529.3646	
Rh	45	(Kr) $4d_-^4$ $4d_+^4$ $5s_+^1$	$\underline{4782.7806}$	$\underline{4782.7917}$	(Kr) $4d^8$ $5s^1$ c)
		(Kr) $4d_-^4$ $4d_+^5$	4782.7568	4782.7632	
		(Kr) $4d_-^4$ $4d_+^3$ $5s_+^2$	4782.7094	4782.7226	

Table 5 (continued)

Symbol	Z	Electron structure	DHF calculated		Ground state
			– TE(AU)	– AE(AU)	[28], c) [2] d) [9]
Pd	46	(Kr) $4d_-^4$ $4d_+^5$ $5s_+^1$	5044.5316	5044.5390	c)
		(Kr) $4d_-^4$ $4d_+^6$	5044.5269	5044.5269	(Kr) $4d^{10}$
		(Kr) $4d_-^4$ $4d_+^4$ $5s_+^2$	5044.4352	5044.4477	
Ag	47	(Kr) $4d_-^4$ $4d_+^6$ $5s_+^1$	5314.7757	5314.7757	(Kr) $4d^{10}$ $5s^1$ c)
		(Kr) $4d_-^4$ $4d_+^6$ $5p_-^1$	5314.6644	5314.6644	
		(Kr) $4d_-^4$ $4d_+^5$ $5s_+^2$	5314.6508	5314.6590	
Cd	48	(Kr) $4d_-^4$ $4d_+^6$ $5s_+^2$	5593.4802	5593.4802	(Kr) $4d^{10}$ $5s^2$ c)
		(Kr) $4d_-^4$ $4d_+^6$ $5s_+^1$ $5p_-^1$	5593.3640	5593.3640	
		(Kr) $4d_-^4$ $4d_+^5$ $5s_+^2$ $5p_-^1$	5593.0917	5593.1007	
In	49	$(4d^{10})$ $5s_+^2$ $5p_-^1$	5880.6194	5880.6194	(Cd) $5p^1$
		$(4d^{10})$ $5s_+^1$ $5p_-^2$	5880.4324	5880.4324	
Sn	50	$(4d^{10})$ $5s_+^2$ $5p_-^2$	6176.3416	6176.3416	(Cd) $5p^2$
		$(4d^{10})$ $5s_+^1$ $5p_-^2$ $5p_+^1$	6176.0967	6176.1004	
Sb	51	$(4d^{10})$ $5s_+^2$ $5p_-^2$ $5p_+^1$	6480.7646	6480.7686	(Cd) $5p^3$
		$(4d^{10})$ $5s_+^1$ $5p_-^2$ $5p_+^2$	6480.4471	6480.4525	
Te	52	$(4d^{10})$ $5s_+^2$ $5p_-^2$ $5p_+^2$	6793.9838	6793.9897	(Cd) $5p^4$
		$(4d^{10})$ $5s_+^1$ $5p_-^2$ $5p_+^3$	6793.5842	6793.5887	
I	53	$(4d^{10})$ $5s_+^2$ $5p_-^2$ $5p_+^3$	7116.0977	7116.1025	(Cd) $5p^5$
		$(4d^{10})$ $5s_+^2$ $5p_-^2$ $5p_+^2$ $6s_+^1$	7115.8535	7115.8603	
		$(4d^{10})$ $5s_+^1$ $5p_-^2$ $5p_+^4$	7115.6124	7115.6124	
Xe	54	$(4d^{10})$ $5s_+^2$ $5p_-^2$ $5p_+^4$	7447.2186	7447.2186	(Cd) $5p^6$
		$(4d^{10})$ $5s_+^2$ $5p_-^2$ $5p_+^3$ $6s_+^1$	7446.9369	7446.9424	
		$(4d^{10})$ $5s_+^2$ $5p_-^2$ $5p_+^3$ $5d_-^1$	7446.8801	7446.8869	
Cs	55	(Xe) $6s_+^1$	7787.1333	7787.1333	(Xe) $6s^1$ c)
		(Xe) $5d_-^1$	7787.0727	7787.0763	
Ba	56	(Xe) $6s_+^2$	8136.0530	8136.0530	(Xe) $6s^2$ c)
		(Xe) $5d_-^1$ $6s_+^1$	8136.0154	8136.0185	

Table 5 (continued)

Symbol	Z	Electron structure	DHF calculated		Ground state
			$-$TE(AU)	$-$AE(AU)	[28], c) [2], d) [9]
La	57	(Xe) $5d_-^1$ $6s_+^2$	8494.1045	8494.1086	(Xe) $5d^1$ $6s^2$ c)
		(Xe) $5d_-^2$ $6s_+^1$	8494.0874	8494.0923	
		(Xe) $4f_-^1$ $6s_+^2$	8494.0054	8494.0136	
Hf	72	(Xe) $4f_-^6$ $4f_+^8$ $5d_-^2$ $6s_+^2$	15090.919	15090.926	(Xe) $4f^{14}$ $5d^2$ $6s^2$ c)
		(Xe) $4f_-^6$ $4f_+^8$ $5d_-^3$ $6s_+^1$	15090.837	15090.841	
		(Xe) $4f_-^6$ $4f_+^7$ $5d_-^3$ $6s_+^2$	15090.463	15090.483	
Ta	73	$(4f^{14})$ $5d_-^3$ $6s_+^2$	15619.018	15619.024	(Xe) $4f^{14}$ $5d^3$ $6s^2$ c)
		$(4f^{14})$ $5d_-^4$ $6s_+^1$	15618.957	15618.957	
		$(4f^{14})$ $5d_-^4$ $5d_+^1$	15618.950	15618.952	
W	74	$(4f^{14})$ $5d_-^4$ $6s_+^2$	16158.864	16158.864	(Xe) $4f^{14}$ $5d^4$ $6s^2$
		$(4f^{14})$ $5d_-^4$ $5d_+^1$ $6s_+^1$	16158.809	16158.814	
		(Xe) $4f_-^6$ $4f_+^7$ $5d_-^4$ $5d_+^1$ $6s_+^2$	16157.811	16157.833	
Re	75	$(4f^{14})$ $5d_-^4$ $5d_+^1$ $6s_+^2$	16710.606	16710.612	(Xe) $4f^{14}$ $5d^5$ $6s^2$
		$(4f^{14})$ $5d_-^4$ $5d_+^2$ $6s_+^1$	16710.562	16710.571	c)
		$(4f^{14})$ $5d_-^4$ $5d_+^3$	16710.465	16710.474	
Os	76	$(4f^{14})$ $5d_-^4$ $5d_+^2$ $6s_+^2$	17274.417	17274.427	(Xe) $4f^{14}$ $5d^6$ $6s^2$
		$(4f^{14})$ $5d_-^4$ $5d_+^3$ $6s_+^1$	17274.390	17274.402	c)
		$(4f^{14})$ $5d_-^4$ $5d_+^4$	17274.305	17274.314	
Ir	77	$(4f^{14})$ $5d_-^4$ $5d_+^3$ $6s_+^2$	17850.468	17850.480	(Xe) $4f^{14}$ $5d^7$ $6s^2$ d)
		$(4f^{14})$ $5d_-^4$ $5d_+^4$ $6s_+^1$	17850.459	17850.469	c)
		$(4f^{14})$ $5d_-^4$ $5d_+^5$	17850.393	17850.399	
Pt	78	$(4f^{14})$ $5d_-^4$ $5d_+^5$ $6s_+^1$	18438.953	18438.960	(Xe) $4f^{14}$ $5d^9$ $6s^1$ c) d)
		$(4f^{14})$ $5d_-^4$ $5d_+^4$ $6s_+^2$	18438.937	18438.948	
		$(4f^{14})$ $5d_-^4$ $5d_+^6$	18438.902	18438.902	
Au	79	$(4f^{14})$ $5d_-^4$ $5d_+^6$ $6s_+^1$	19040.044	19040.044	(Xe) $4f^{14}$ $5d^{10}$ $6s^1$ c) d)
		$(4f^{14})$ $5d_-^4$ $5d_+^5$ $6s_+^2$	19040.005	19040.012	
		$(4f^{14})$ $5d_-^4$ $5d_+^6$ $6p_-^1$	19039.895	19039.895	

Table 5 (continued)

Symbol	Z	Electron structure	DHF calculated $-$TE(AU)	 $-$AE(AU)	Ground state [28], c) [2], d) [9]
Hg	80	$(4f^{14})$ $5d_-^4$ $5d_+^6$ $6s_+^2$	19653.870	19653.870	(Xe) $4f^{14}$ $5d^{10}$ $6s^2$
		$(4f^{14})$ $5d_-^4$ $5d_+^6$ $6s_+^1$ $6p_-^1$	19653.713	19653.713	
		$(4f^{14})$ $5d_-^4$ $5d_+^5$ $6s_+^2$ $6p_-^1$	19653.594	19653.602	
Tl	81	$(5d^{10})$ $6s_+^2$ $6p_-^1$	20280.397	20280.397	(Hg) $6p^1$
		$(5d^{10})$ $6s_+^1$ $6p_-^2$	20280.183	20280.183	
Pb	82	$(5d^{10})$ $6s_+^2$ $6p_-^2$	20919.909	20919.909	(Hg) $6p^2$
		$(5d^{10})$ $6s_+^1$ $6p_-^2$ $6p_+^1$	20919.599	20919.602	
		$(5d^{10})$ $5f_-^2$ $6s_+^2$	20919.311	20919.313	
		$(4f^{14})$ $5d_-^4$ $5d_+^5$ $6s_+^2$ $6p_-^2$ $6p_+^2$	20919.276	20919.289	
Bi	83	$(5d^{10})$ $6s_+^2$ $6p_-^2$ $6p_+^1$	21572.572	21572.576	(Hg) $6p^3$
		$(5d^{10})$ $6s_+^1$ $6p_-^2$ $6p_+^2$	21572.177	21572.182	
Po	84	$(5d^{10})$ $6s_+^2$ $6p_-^2$ $6p_+^2$	22238.584	22238.589	(Hg) $6p^4$
		$(5d^{10})$ $6s_+^1$ $6p_-^2$ $6p_+^3$	22238.101	22238.105	
At	85	$(5d^{10})$ $6s_+^2$ $6p_-^2$ $6p_+^3$	22918.167	22918.171	
		$(5d^{10})$ $6s_+^2$ $6p_-^2$ $6p_+^2$ $7s_+^1$	22917.961	22917.967	
		$(5d^{10})$ $6s_+^1$ $6p_-^2$ $6p_+^4$	22917.583	22917.583	
Rn	86	$(5d^{10})$ $6s_+^2$ $6p_-^2$ $6p_+^4$	23611.517	23611.517	(Hg) $6p^6$
		$(5d^{10})$ $6s_+^2$ $6p_-^2$ $6p_+^3$ $7s_+^1$	23611.289	23611.294	
		$(5d^{10})$ $6s_+^2$ $6p_-^2$ $6p_+^3$ $6d_-^1$	23611.225	23611.231	
Fr	87	(Rn) $7s_+^1$	24318.616	24318.616	c)
		(Rn) $6d_-^1$	24318.557	24318.558	
Ra	88	(Rn) $7s_+^2$	25039.773	25039.773	(Rn) $7s^2$
		(Rn) $6d_-^1$ $7s_+^1$	25039.719	25039.722	
		(Rn) $7s_+^1$ $7p_-^1$	25039.719	25039.719	
Ac	89	(Rn) $6d_-^1$ $7s_+^2$	25775.221	25775.224	(Rn) $6d^1$ $7s^2$
		(Rn) $6d_-^2$ $7s_+^1$	25775.165	25775.169	

Table 5 (continued)

Symbol	Z	Electron structure	DHF calculated $-$TE(AU)	DHF calculated $-$AE(AU)	Ground state [28], c) [2] d) [9]
	104	$(5f^{14})\ 6d_-^1\ 7s_+^2\ 7p_-^1$	$\underline{38758.899}$	$\underline{38758.903}$	
		$(5f^{14})\ 6d_-^2\ 7s_+^2$	38758.894	38758.899	d)
		$(5f^{14})\ 7s_+^2\ 7p_-^2$	38758.831	38758.831	
		$(5f^{14})\ 6d_-^3\ 7s_+^1$	38758.776	38758.780	
		$(5f^{14})\ 6d_-^1\ 7s_+^1\ 7p_-^2$	38758.758	38758.763	
		$(\mathrm{Rn})\ 5f_-^6\ 5f_+^7\ 6d_-^3\ 7s_+^2$	38758.436	38758.451	
	105	$(5f^{14})\ 6d_-^3\ 7s_+^2$	$\underline{39772.180}$	$\underline{39772.185}$	d)
		$(5f^{14})\ 6d_-^2\ 7s_+^2\ 7p_-^1$	39772.163	39772.169	
		$(5f^{14})\ 6d_-^1\ 7s_+^2\ 7p_-^2$	39772.076	39772.081	
		$(5f^{14})\ 6d_-^4\ 7s_+^1$	39772.070	39772.070	
	106	$(5f^{14})\ 6d_-^4\ 7s_+^2$	$\underline{40806.599}$	$\underline{40806.599}$	d)
		$(5f^{14})\ 6d_-^4\ 6d_+^1\ 7s_+^1$	40806.473	40806.477	
		$(\mathrm{Rn})\ 5f_-^6\ 5f_+^7\ 6d_-^4\ 6d_+^1\ 7s_+^2$	40805.719	40805.735	
	107	$(5f^{14})\ 6d_-^4\ 6d_+^1\ 7s_+^2$	$\underline{41862.784}$	$\underline{41862.789}$	d)
		$(5f^{14})\ 6d_-^4\ 6d_+^2\ 7s_+^1$	41862.646	41862.654	
		$(5f^{14})\ 6d_-^4\ 6d_+^3$	41862.484	41862.492	
	108	$(5f^{14})\ 6d_-^4\ 6d_+^2\ 7s_+^2$	$\underline{42941.395}$	$\underline{42941.403}$	d)
		$(5f^{14})\ 6d_-^4\ 6d_+^3\ 7s_+^1$	42941.260	42941.269	
		$(5f^{14})\ 6d_-^4\ 6d_+^4$	42941.100	42941.108	
	109	$(5f^{14})\ 6d_-^4\ 6d_+^3\ 7s_+^2$	$\underline{44043.206}$	$\underline{44043.216}$	d)
		$(5f^{14})\ 6d_-^4\ 6d_+^4\ 7s_+^1$	44043.088	44043.097	
		$(5f^{14})\ 6d_-^4\ 6d_+^5$	44042.923	44042.928	
	110	$(5f^{14})\ 6d_-^4\ 6d_+^4\ 7s_+^2$	$\underline{45169.029}$	$\underline{45169.038}$	d)
		$(5f^{14})\ 6d_-^4\ 6d_+^5\ 7s_+^1$	45168.909	45168.915	
		$(5f^{14})\ 6d_-^4\ 6d_+^6$	45168.749	45168.749	c)
	111	$(5f^{14})\ 6d_-^4\ 6d_+^5\ 7s_+^2$	$\underline{46319.724}$	$\underline{46319.730}$	d)
		$(5f^{14})\ 6d_-^4\ 6d_+^6\ 7s_+^1$	46319.621	46319.621	c)
		$(5f^{14})\ 6d_-^4\ 6d_+^6\ 7p_-^1$	46319.385	46319.385	

Table 5 (continued)

Symbol	Z	Electron structure		DHF calculated −TE(AU)	DHF calculated −AE(AU)	Ground state [28], c) [2] d) [9]
	112	$(5f^{14})$	$6d_-^4\ 6d_+^6\ 7s_+^2$	$\underline{47496.244}$	$\underline{47496.244}$	d)
		$(5f^{14})$	$6d_-^4\ 6d_+^5\ 7s_+^2\ 7p_-^1$	47496.125	47496.132	
		$(5f^{14})$	$6d_-^4\ 6d_+^6\ 7s_+^1\ 7p_-^1$	47496.026	47496.026	
	113	$(6d^{10})$	$7s_+^2\ 7p_-^1$	$\underline{48699.491}$	$\underline{48699.491}$	d)
		$(6d^{10})$	$7s_+^1\ 7p_-^2$	48699.198	48699.198	
		$(6d^{10})$	$7s_+^1\ 7p_-^1\ 7p_+^1$	48699.101	48699.104	
	114	$(6d^{10})$	$7s_+^2\ 7p_-^2$	$\underline{49930.620}$	$\underline{49930.620}$	d)
		$(5f^{14})$	$6d_-^4\ 6d_+^5\ 7s_+^2\ 7p_-^2\ 7p_+^1$	49930.202	49930.213	
		$(6d^{10})$	$7s_+^1\ 7p_-^2\ 7p_+^1$	49930.160	49930.163	
		$(6d^{10})$	$7s_+^2\ 6f_-^2$	49929.888	49929.890	
	115	$(6d^{10})$	$7s_+^2\ 7p_-^2\ 7p_+^1$	$\underline{51190.773}$	$\underline{51190.776}$	d)
		$(6d^{10})$	$7s_+^1\ 7p_-^2\ 7p_+^2$	51190.165	51190.169	
	116	$(6d^{10})$	$7s_+^2\ 7p_-^2\ 7p_+^2$	$\underline{52481.367}$	$\underline{52481.372}$	d)
		$(6d^{10})$	$7s_+^1\ 7p_-^2\ 7p_+^3$	52480.659	52480.663	
	117	$(6d^{10})$	$7s_+^2\ 7p_-^2\ 7p_+^3$	$\underline{53803.978}$	$\underline{53803.982}$	d)
		$(6d^{10})$	$7s_+^2\ 7p_-^2\ 7p_+^2\ 8s_+^1$	53803.873	53803.878	
		$(6d^{10})$	$7s_+^1\ 7p_-^2\ 7p_+^4$	53803.123	53803.123	
	118	$(6d^{10})$	$7s_+^2\ 7p_-^2\ 7p_+^4$	$\underline{55160.323}$	$\underline{55160.323}$	d)
		$(6d^{10})$	$7s_+^2\ 7p_-^2\ 7p_+^3\ 8s_+^1$	55160.206	55160.210	
		$(6d^{10})$	$7s_+^2\ 7p_-^2\ 7p_+^3\ 7d_-^1$	55160.108	55160.114	
	119	(118)	$8s_+^1$	$\underline{56552.178}$	$\underline{56552.178}$	d)
		(118)	$7d_-^1$	56552.081	56552.083	
		(118)	$8p_-^1$	56551.774	56551.774	
	120	(118)	$8s_+^2$	$\underline{57981.806}$	$\underline{57981.806}$	
		(118)	$8s_+^1\ 8p_-^1$	57981.738	57981.738	
		(118)	$8s_+^1\ 7d_-^1$	57981.707	57981.709	

When only one accepted electron structure for an atomic number Z was calculated [2], entries c) in Table 5 were omitted.

Table 5: the calculated TE and AE for all elements up to $Z=120$. Each element was calculated in two or more electron configurations. In Table 5 when only one configuration is presented (case Li, Be, Na, K), the second calculated configuration was not converging.

Table 5 contains all chemical periods from H up to $Z=120$; lanthanides and actinides are separated from other elements in Tables 6, 7. Symbol and Z in the first two columns are self-explanatory. Electron structure in the third column of Table 5 is denoted by n, l, a symbols for the last electrons which follow the electron configuration of a core with all closed shells. As cores the symbols (Ne), (Ar), (Kr), (Xe), (Rn), (118) are used for the configuration of ground states of elements Ne, Ar, Kr, Xe, Rn and 118. When symbols ($3d^{10}$), ($4d^{10}$), ($4f^{14}$), ($5d^{10}$), ($5f^{14}$) and ($6d^{10}$) are used, they correspond to closed shell configurations of (Ar) $3d_-^4\ 3d_+^6$, (Kr) $4d_-^4\ 4d_+^6$, (Xe) $4f_-^6\ 4f_+^8$, (Xe) $4f_-^6\ 4f_+^8\ 5d_-^4\ 5d_+^6$, (Rn) $5f_-^6\ 5f_+^8$ and (Rn) $5f_-^6\ 5f_+^8\ 6d_-^4\ 6d_+^6$, respectively.

In columns 4 and 5 our calculated values in atomic units taken with – sign are presented. The value with the lowest energy among them is underlined, corresponding to our calculated ground states. In the last column experimentally known ground states spectroscopically determined up to $Z=96$ are presented – according to [28], by non-relativistic symbols similar to relativistic ones in column 3. Besides the cores of noble gases, here we use (Zn), (Ce) and (Hg), each corresponding to the electron ground states of Zn, Cd or Hg respectively for cores.

In the last column, when available, the ground state determined by NRHF calculations according to [2] is marked by the symbol *c*). Also, when available, the gound state determined by DFS according to [9] is marked by the symbol *d*). In the case of lanthanides (Table 6) full TE values calculated in [2] are presented. In the case of actinides (Table 7) our results are compared with full NRHF data from [2] and DFS data from [9] and are discussed in the following section.

4. Discussion

Table 5 presents our results for total energies (– TE or – AU) of all elements in the periodic system up to $Z=120$ (exclusive of $4f$ and $5f$ elements) in comparison with spectroscopically determined ground states of [28]. It is visible that our calculated ground states as TE or AE (under-lined in Table 5) show the same electron structure. One exclusion is the case of Mo, where TE shows (Kr) $4d_-^4\ 5s_+^2$ structure and AE (Kr) $4d_-^4\ 4d_+^1\ 5s_+^1$ structure. However, energetically, they are within the limits of calculating errors and are, therefore, equally possible. The errors of calculation, taken as the difference between two calculations repeated in sequence (using the first results as the starting point for the second calculation) is usually $\pm\ 0.001-0.002$ AU. In comparison with experimentally determined ground states, our results in Table 5 reproduce them completely, with the following few exclusions: Cr, Cu, Nb, Tc, Pd. It is necessary to bear in mind that experimentally the ground state is determined as the electron structure giving the lowest lying multiplet. Our program is able to calculate only a mean energetic level of each configuration (AE), i.e., the barycentrum of all multiplets of the determined ground state configuration. If two configurations exist with a

Table 6. Total energies of lanthanides in AU($-E_T$ values)

Symbol	Z	Electron structure	This work ($-$TE)	DHF ($-$AE)	NR $-$ HF [2]	NR $-$ H [2]	Experimental [28] ground state
La	57	(Xe) $5d_-^1\ 6s_+^2$	8494.1045*	8494.1086*	8220.473*	8141.964*	(Xe) $5d^1\ 6s^2$
		(Xe) $5d_-^2\ 6s_-^1$	8494.0874	8494.0923			
		(Xe) $4f_-^1\ 6s_+^2$	8494.0054	8494.0137	8220.291	8141.887	
Ce	58	(Xe) $4f_-^1\ 5d_-^1\ 6s_+^2$	8861.5974*	8861.6117*	8566.201*	8484.990*	(Xe) $4f^1\ 5d^1\ 6s^2$
		(Xe) $4f_-^2\ 6s_+^2$	8861.5277	8861.5422	8566.109	8484.834	
		(Xe) $5d_-^2\ 6s_+^2$	8861.4690	8861.4751	8565.985	8484.976	
Pr	59	(Xe) $4f_-^2\ 5d_-^1\ 6s_+^2$	9238.8064*	9238.8278*	8920.320	8836.331*	
		(Xe) $4f_-^3\ 6s_+^2$	9238.7565	9238.7738	8920.324*	8836.200	(Xe) $4f^3\ 6s^2$
		(Xe) $4f_-^1\ 5d_-^2\ 6s_+^2$	9238.6512	9238.6689	8920.076	8836.275	
		(Xe) $5d_-^3\ 6s_+^2$			8919.610	8836.031	
Nd	60	(Xe) $4f_-^3\ 5d_-^1\ 6s_+^2$	9625.8666*	9625.8910*	9282.884	9196.042*	
		(Xe) $4f_-^4\ 6s_+^2$	9625.8381	9625.8544	9282.909*	9195.923	(Xe) $4f^4\ 6s^2$
		(Xe) $4f_-^2\ 5d_-^2\ 6s_+^2$	9625.6908	9625.7163			
Pm	61	(Xe) $4f_-^4\ 5d_-^1\ 6s_+^2$	10022.9266*	10022.9495*	9653.980	9564.213*	
		(Xe) $4f_-^5\ 6s_+^2$	10022.9133	10022.9240	9654.023*	9564.103	(Xe) $4f^5\ 6s^2$
		(Xe) $4f_-^3\ 5d_-^2\ 6s_+^2$	10022.7258	10022.7544			
Sm	62	(Xe) $4f_-^6\ 6s_+^2$	10430.1302*	10430.1302	10033.732*	9940.806	(Xe) $4f^6\ 6s^2$
		(Xe) $4f_-^5\ 5d_-^1\ 6s_+^2$	10430.1179	10430.1343*	10033.674	9940.910*	
		(Xe) $4f_-^4\ 5d_-^2\ 6s_+^2$	10429.9022	10429.9291			
Eu	63	(Xe) $4f_-^6\ 5d_-^1\ 6s_+^2$	10847.6027*	10847.6072*	10422.037	10326.204*	
		(Xe) $4f_-^6\ 4f_+^1\ 6s_+^2$	10847.5153	10847.5247	10422.108*	10326.107	(Xe) $4f^7\ 6s^2$
		(Xe) $4f_-^5\ 4f_+^2\ 6s_+^2$	10847.4429	10847.4709			
		(Xe) $4f_-^5\ 5d_-^2\ 6s_+^2$	10847.3660	10847.3856			
Gd	64	(Xe) $4f_-^6\ 4f_+^1\ 5d_-^1\ 6s_+^2$	11275.3958*	11275.4109*	10819.139	10720.165*	(Xe) $4f^7\ 5d^1\ 6s^2$
		(Xe) $4f_-^6\ 4f_+^2\ 6s_+^2$	11275.3201	11275.3370	10819.225*	10720.075	
		(Xe) $4f_-^6\ 5d_-^2\ 6s_+^2$	11275.2588	11275.2654			

Table 6 (continued)

Symbol	Z	Electron structure	This work (−TE)	DHF (−AE)	NR − HF [2]	NR − H [2]	Experimental [28] ground state
Tb	65	(Xe) $4f^6_- \ 4f^2_+ \ 5d^1_- \ 6s^2_+$	11713.7535*	11713.7769*	11225.080	11122.892*	
		(Xe) $4f^6_- \ 4f^3_+ \ 6s^2_+$	11713.6898	11713.7118	11225.175*	11122.803	(Xe) $4f^9$ $6s^2$
		(Xe) $4f^6_- \ 4f^1_+ \ 5d^2_- \ 6s^2_+$	11713.6038	11713.6221	11224.741	11122.765	
Dy	66	(Xe) $4f^6_- \ 4f^3_+ \ 5d^1_- \ 6s^2_+$	12162.8253*	12162.8542*	11639.912	11534.437*	
		(Xe) $4f^6_- \ 4f^4_+ \ 6s^2_+$	12162.7717	12162.7960	11640.014*	11534.349	(Xe) $4f^{10}$ $6s^2$
		(Xe) $4f^6_- \ 4f^2_+ \ 5d^2_- \ 6s^2_+$	12162.6650	12162.6924			
Ho	67	(Xe) $4f^6_- \ 4f^4_+ \ 5d^1_- \ 6s^2_+$	12622.7719*	12622.8030*	12063.708	11954.872*	
		(Xe) $4f^6_- \ 4f^5_+ \ 6s^2_+$	12622.7266	12622.7500	12063.818*	11954.784	(Xe) $4f^{11}$ $6s^2$
		(Xe) $4f^6_- \ 4f^3_+ \ 5d^2_- \ 6s^2_+$	12622.5966	12622.6298			
Er	68	(Xe) $4f^6_- \ 4f^5_+ \ 5d^1_- \ 6s^2_+$	13093.7330*	13093.7632*	12496.560	12384.288*	
		(Xe) $4f^6_- \ 4f^6_+ \ 6s^2_+$	13093.7018	13093.7211	12496.673*	12384.196	(Xe) $4f^{12}$ $6s^2$
		(Xe) $4f^6_- \ 4f^4_+ \ 5d^2_- \ 6s^2_+$	13093.5581	13093.5581			
Tm	69	(Xe) $4f^6_- \ 4f^6_+ \ 5d^1 \ 6s^2_+$	13575.8969*	13575.9224*	12938.520	12822.738*	
		(Xe) $4f^6_- \ 4f^7_+ \ 6s^2_+$	13575.8540	13575.8656	12938.633*	12822.647	(Xe) $4f^{13}$ $6s^2$
		(Xe) $4f^6_- \ 4f^5_+ \ 5d^2_- \ 6s^2_+$	13575.7059	13575.7404			
Yb	70	(Xe) $4f^6_- \ 4f^7_+ \ 5d^1_- \ 6s^2_+$	14069.4034*	14069.4203*	13389.685	13270.315*	
		(Xe) $4f^6_- \ 4f^8_+ \ 6s^2_+$	14069.3615	14069.3615	13389.800*	13270.209	(Xe) $4f^{14}$ $6s^2$
		(Xe) $4f^6_- \ 4f^6_+ \ 5d^2_- \ 6s^2_+$	14069.2041	14069.2335			
Lu	71	(Xe) $4f^6_- \ 4f^8_+ \ 5d^1_- \ 6s^2_+$	14574.4121*	14574.4164*	13850.105*	13727.072*	(Xe) $4f^{14}$ $5d^1$ $6s^2$
		(Xe) $4f^6_- \ 4f^8_+ \ 5d^2_- \ 6s^1_+$	14574.3276	14574.3324	13850.022	13736.962	
		(Xe) $4f^6_- \ 4f^7_+ \ 5d^2_- \ 6s^2_+$	14574.2155	14574.2356			

Table 7. Total energies of actinides in AU($-E$ values)

Symbol	Z	Electron structure	This work (−TE)	DHF (−AE)	DFS Finite nucleus [9]	NR−HF [2]	NR−H [2]	Experimental [28, 30] ground state
Ac	89	(Rn) $6d_-^1\ 7s_+^2$	25775.221*	25775.224*	25748.8215*	23719.989	23529.981	(Rn) $6d^1\ 7s^2$
		(Rn) $6d_-^2\ 7s_-^1$	25775.165	25775.169				
		(Rn) $5f_-^1\ 7s_+^2$	not converging		25748.7235			
Th	90	(Rn) $6d_-^2\ 7s_+^2$	26525.270*	26525.275*	26497.1235*	24357.353	24163.507*	(Rn) $6d^2\ 7s^2$
		(Rn) $5f_-^1\ 6d_-^1\ 7s_+^2$	26525.195	26525.205	26497.102	24357.453*	24163.481	
		(Rn) $5f_-^2\ 7s_+^2$	26525.088	26525.097	26497.036	24357.425	24163.377	
Pa	91	(Rn) $5f_-^1\ 6d_-^2\ 7s_+^2$	27290.293*	27290.306*	27260.451	25004.576	24806.696	
		(Rn) $5f_-^2\ 6d_-^1\ 7s_+^2$	27290.261	27290.276	27260.473*	25004.724	24806.714*	(Rn) $5f^2\ 6d^1\ 7s^2$
		(Rn) $5f_-^2\ 6d_-^2\ 7s_+^1$	27290.221	27290.237				
		(Rn) $6d_-^3\ 7s_+^2$	27290.212	27290.216				
		(Rn) $5f_-^3\ 7s_+^2$	27290.148	27290.160	27290.237	25004.746*	24806.641	
U	92	(Rn) $5f_-^3\ 6d_-^1\ 7s_+^2$	28070.689*	28070.707*	28038.6875*	25661.828	25459.711*	(Rn) $5f^3\ 6d^1\ 7s^2$
		(Rn) $5f_-^2\ 6d_-^2\ 7s_+^2$	28070.672	28070.690	28038.6235	25661.628	25459.651	
		(Rn) $5f_-^4\ 7s_+^2$	28070.613	28070.624	28038.680	25661.887*	25459.660	
		(Rn) $5f_-^1\ 6d_-^3\ 7s_+^2$	28070.547	28070.560				
Np	93	(Rn) $5f_-^4\ 6d_-^1\ 7s_+^2$	28866.774*	28866.791*	28832.6635	26328.820	26122.532*	(Rn) $5f^4\ 6d^1\ 7s^2$
		(Rn) $5f_-^5\ 7s_+^2$	28866.722	28866.730	28832.6845*	26328.930*	26122.519	
		(Rn) $5f_-^3\ 6d_-^2\ 7s_+^2$	28866.711	28866.732	28832.563	26328.590	26122.458	
Pu	94	(Rn) $5f_-^5\ 6d_-^1\ 7s_+^2$	29678.838*	29678.850*	29642.1245	27005.753	26795.231	
		(Rn) $5f_-^6\ 7s_+^2$	29678.812	29678.812	29642.176*	27005.911*	26795.252*	(Rn) $5f^6\ 7s^2$
		(Rn) $5f_-^4\ 6d_-^2\ 7s_+^2$	29678.747	29678.767	29641.987	27005.481	26795.114	
Am	95	(Rn) $5f_-^6\ 6d_-^1\ 7s_+^2$	30507.231*	30507.235*	30467.781	27692.695	27477.876	
		(Rn) $5f_-^6\ 5f_+^1\ 7s_+^2$	30507.135	30507.142	30467.8205*	27692.884*	27477.916*	(Rn) $5f^7\ 7s^2$
		(Rn) $5f_-^5\ 6d_-^2\ 7s_+^2$	30507.109	30507.124	30467.608	27692.366	27477.713	

Table 7 (continued)

Symbol	Z	Electron structure	This work (− TE)	DHF (− AE)	DFS Finite nucleus [9]	NR−HF [2]	NR−H [2]	Experimental [28, 30] ground state
Cm	96	(Rn) $5f_-^6\ 5f_+^1\ 6d_-^1\ 7s_+^2$	31352.179*	31352.191*	31309.039	28389.681	28170.503	(Rn) $5f^7\ 6d^1\ 7s^2$
		(Rn) $5f_-^6\ 6d_-^2\ 7s_+^2$	31352.133	31352.139	31308.881	28389.304	28170.301	
		(Rn) $5f_-^6\ 5f_+^2\ 7s_+^2$	31352.116	31352.128	31309.1055*	28389.907*	28170.569*	
Bk	97	(Rn) $5f_-^6\ 5f_+^2\ 6d_-^1\ 7s_+^2$	32215.135*	32214.152*	32167.4905	29096.792	28872.193	
		(Rn) $5f_-^6\ 5f_+^3\ 7s_+^2$	32214.106	32214.122	32167.5805*	29097.055*	28873.282*	
		(Rn) $5f_-^6\ 5f_+^1\ 6d_-^2\ 7s_+^2$	32214.053	32214.067	32167.301	29096.376	28872.962	
		(Rn) $5f_-^6\ 5f_+^4\ 7s_+^1$	32213.894	32213.909				
Cf	98	(Rn) $5f_-^6\ 5f_+^4\ 7s_+^2$	33093.492*	33093.510*	33043.7585*	29814.350*	29586.081*	
		(Rn) $5f_-^6\ 5f_+^3\ 6d_-^1\ 7s_+^2$	33093.475	33093.496	33043.642	29814.037	29585.955	
		(Rn) $5f_-^6\ 5f_+^2\ 6d_-^2\ 7s_+^2$	33093.377	33093.397	33043.423			
Es	99	(Rn) $5f_-^6\ 5f_+^5\ 7s_+^2$	33990.664*	33990.681*	33936.8105*	30541.883*	30309.055*	
		(Rn) $5f_-^6\ 5f_+^4\ 6d_-^1\ 7s_+^2$	33990.643	33990.666	33936.6725	30541.541	30308.912	
		(Rn) $5f_-^6\ 5f_+^3\ 6d_-^2\ 7s_+^2$	33990.497	33990.522	33936.4235			
Fm	100	(Rn) $5f_-^6\ 5f_+^6\ 7s_+^2$	34906.063*	34906.077*	34847.5135*	31279.643*	31042.192*	
		(Rn) $5f_-^6\ 5f_+^5\ 6d_-^1\ 7s_+^2$	34906.019	34906.041	34847.352	31279.253	31042.014	
		(Rn) $5f_-^6\ 5f_+^7\ 7s_+^1$	34905.868	34905.876				
		(Rn) $5f_-^6\ 5f_+^4\ 6d_-^2\ 7s_+^2$	34905.851	34905.878	34847.0745			
Md	101	(Rn) $5f_-^6\ 5f_+^7\ 7s_+^2$	35840.177*	35840.186*	35776.1305*	32027.727*	31785.589*	
		(Rn) $5f_-^6\ 5f_+^6\ 6d_-^1\ 7s_+^2$	35840.094	35840.113	35775.948	32027.327	31785.414	
		(Rn) $5f_-^6\ 5f_+^8\ 7s_+^1$	35839.979	35839.979				
		(Rn) $5f_-^6\ 5f_+^5\ 6d_-^2\ 7s_+^2$	35839.869	35839.895	35775.6415			
No	102	(Rn) $5f_-^6\ 5f_+^8\ 7s_+^2$	36793.382*	36793.382*	36721.740*	32786.180*	32539.291*	
		(Rn) $5f_-^6\ 5f_+^7\ 6d_-^1\ 7s_+^2$	36793.300	36793.313	36721.533	32785.739	32539.087	
		(Rn) $5f_-^6\ 5f_+^6\ 6d_-^2\ 7s_+^2$	36793.048	36793.060	36721.1985			
Lr	103	(Rn) $5f_-^6\ 5f_+^8\ 6d_-^1\ 7s_+^2$	37766.134*	37766.138*	37682.363	33554.555	33303.099	
		(Rn) $5f_-^6\ 5f_+^8\ 6d_-^2\ 7s_+^1$	37766.025	37766.030				
		(Rn) $5f_-^6\ 5f_+^7\ 6d_-^2\ 7s_+^2$	37765.893	37765.909				

close barycentrum of their multiplets (e.g. a difference of only 0.01 AU = 0.27 eV) it is possible that the lowest lying multiplet is in the configuration with the higher lying barycentrum. Furthermore, our calculations for open shells are in error, using coefficients $\Gamma_{j_A v j_B}$ (valid exactly only for closed shells). The magnitude of error introduced by such approximation is visible if we compare our TE with AE, both of which are calculated with different coefficients in the terms containing $\Gamma_{j_A v j_A}$. In the case of Cr, Cu, Nb, Tc and Pd, the maximal difference between TE and AE is 0.011 AU – so here we could accept ± 0.013 AU as a reasonably estimated error in total energy (covering incorrect $\Gamma_{j_A v j_B}$ coefficients and including calculation errors). From this point of view the experimental and theoretical ground states of Cu, Nb, Tc and Pd which differ less than 0.026 AU are still within the ± 0.013 AU error limits. Only the case of Cr clearly indicates some discrepancy between experiment and theory. On the other hand, in almost all cases in Table 5 it is visible that the use of incorrect $\Gamma_{j_A v j_B}$ coefficients in the last few open shells is not very critical because ground states here were correctly calculated. The ground state position found by NRH in [2], available for most of the periodic system (denoted by *c*)) in Table 5, are in accord with our DHF values, including the cases of Cr, Cu, Nb, Tc, Pd – however, they differ in the cases of Re, Os, Ir, 110 and 111 element. The positions of ground states found by DFS calculations [9] (using finite nucleus approximation denoted by *d*)) in Table 5 for Ir, Pt, Au and 105-120 element agree exactly with ours. For 104 element DFS values [9] present $(5f^{14})\,6d_-^2\,7s_+^2$, as the ground state configuration. However, in [9] $(5f^{14})\,6d_-^1\,7s_+^2\,7p_-^1$ state was not calculated by the DFS method which we found to be the ground state. The same ground state as ours was reported by Mann [29].

In contrast to the good accord of calculated ground state with experimental ones in Table 5, the case of lanthanides and actinides in Tables 6 and 7 presents systematical discrepancies. The lowest lying states calculated as DHF (this work), DFS (9), NRH (2) and NRHF (2) in Tables 6 and 7 are denoted by *. From the comparison of our – TE and – AU values in the lanthanides series with spectroscopic data [28, 30], our results of – AE show one $5d_-^1$ electron present in all lanthanides. Our results of – TE indicate the same, with the exclusion of Sm^{62}, where no $5d_-^1$ is present in the ground state. If we accept the value ± 0.02 AU (i.e., maximal allowed difference between two states 0.04 AU) as a reasonably estimated error of – AE or – TE – due to computing errors and incorrect use of $\Gamma_{j_A v j_B}$ also for open shells – we could explain the discrepancy between theory and experiment in the case of Pm and Sm and, perhaps, for Nd and Er. The discrepancies are to great in the cases of Tb, Dy, Ho and especially, of Eu. It is very difficult to explain them in the same way; their calculated ground states, each containing one $5d_-^1$ electron are 0.05 to 0.085 AU lower than states without $5d$ electrons.

In the lanthanide series the positions of ground states from NRH calculations [2] are in exact accord with ours. On the other hand the NRHF calculations [2] are apparently giving wrong results (see Table 6 and Table 7) they are systematically indicating the same structure in both lanthanides and actinides: no $5d_-^1$ electrons in any lanthanide below Ce and no $6d_-^1$ electrons below Th, with similar structure of Ce and Th, each containing one $5d_-^1$ or $6d_-^1$ electron respectively. Systematic DFS results for lanthanides are not available. Our results in the actinide series for both $-$TE or $-$AE values are in accord with experimentaly determined ground state positions for Ac, Th, U, Np and Cm. For Pa and Pu our calculated ground states are 0.03 AU or 0.038 AU lower than those experimentally determined (i.e. still within the estimated 0.04 AU difference, as mentioned in the lanthanide case). In the case of Am (also of Eu) we have a strong discrepancy with experimental results (we found $5d^1_-$ present in the ground state). In the region from Cf to No our results indicate the absence of $6d$ electrons and again the presence of one $6d^1_-$ electron in Lr. DFS results, calculated for actinides in [9], agree with experimental results in the case of Ac, Th, Pa, U, Pu, Am and disagree for Np and Cm. DFS calculations indicate the absence of $6d$ electrons in all actinides, starting from Np. NRH calculations are in the best accord with experiments agreeing in the cases of Ac, Th, Pa, U, Np, Pu and Am and disagreeing for Cm. They indicate the absence of $6d$ electrons in the actinide series starting from Pu.

Generally, the disagreement in the lanthanides and some actinides between calculated and spectroscopically determined ground states known to us from 1969 [16] is disturbing. We realize that it is very important to remove these discrepancies. The most simple way to do it is to find the exact position of both barycentrums in the two neighbor configurations (of experimental ground state and DHF ground state). This can be done by finding its experimental average energies – as the weighted average energetic position of all their multiplets (using the present assignment of spectral lines). This could lead to a natural explanation of discrepancies – without necessitating the reclassification of spectral lines. Another way is to calculate exactly the ground state configuration terms, using the exact complicated coefficients for open shells, in place of $\Gamma_{j_A v j_B}$. This method should give final results, and could, eventually, suggest some need for the change in the ground state assignment of some lanthanides and actinides. However, it needs substantial change in our program and extensive computer time. From this point of view, the present predictions of chemistry of superheavy elements [9, 29], based on DFS [9] and DHF [19] calculations (using calculations of barycentrum of ground state only) are only preliminary – as is natural for the first step in the unknown region. We believe that a thorough investigation of atoms and ions in the known region of the periodic system is crucial in order to predict the chemistry of some superheavy elements by the DHF or DFS methods.

Acknowledgement. The authors are indebted to Professor G. Bouissières for discussions and continuous support of this work.

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