# SCF Dirac-Hartree-Fock Calculations in the Periodic System

## II. Binding Energies and First Ionization Potentials for $s$, $p$, and $d$ Elements from $Z = 1$ to $Z = 120$

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Binding energies calculated by DHF method were compared with modified DFS method calculations and experimental values. First ionization potentials of all elements from $Z = 1$ to $Z = 120$ (excluding the lanthanide and actinide series) were obtained from DHF values. These calculated values were compared with spectroscopically determined first ionization potentials for the region $Z = 1$ to $Z = 88$. The obtained ratios of DHF calculated and experimental values in the $Z \leqq 88$ region (correlation ratios) were extrapolated for $104 - 120$ elements and used in correcting calculated DHF eigenvalues to obtain expected values for the first ionization potential in this region.

## 1. Introduction

Calculations have recently been published to the first ionization potentials of $104 - 120$ element and $156 - 172$ element [1, 2] (together with data for Ir, Os, Au and Hg), derived from the values of Dirac-Fock-Slater (DFS) calculations.

In our previous work we published calculations of all elements from $Z = 1$ to $Z = 120$, using the more complex Dirac-Hartree-Fock method (DHF) [3].

The accuracy of the DHF method is generally greater than that of the DFS method used in [1] and [2], therefore, the comparison of the first ionization potentials from both methods is valuable. Having eigenvalues for all elements from H to 120 element from our DHF calculations, we also performed a number of additional calculations in the known regions, checking the accuracy of our calculation of binding energies from different subshells by two usual methods: as eigenvalues (method A) and as the difference between total energies of the $1^+$ ion and atom (method B). Comparison of our values with those from modified DFS method [4] is also of interest.

This work, as part of our study of the periodic system by the DHF method, is based on the idea that any valuable extrapolation in unknown parts of the periodic system (beyond $Z > 103$) must be supported by extensive calculations in the known region, using the same computer program.

## 2. Eigenvalues and Binding Energies

The general DHF method, as derived for many electron atoms [5, 6, 8] solves a set of integro-differential DHF equations including electric, magnetic and retardation interaction of each electron with all electrons. In this method the ionization potential (i.e. the electrons binding energy on each subshell with a given set of quantum numbers $(n, l, j)$, is directly equal to the eigenvalue $\varepsilon_{nlj} = B_{nlj}$. This supposes that removing an electron from the $(n, l, j)$ subshell does not affect the other subshells (method of "frozen orbitals" according to Koopman's theorem [7]). This method we will refer to as "method A". The other method is that of calculating binding energy $B_{nlj}$ as the difference between the total energy of the atom and corresponding $1^+$ ion. This method, which we will refer to as "method B", includes rearranging effects on energy levels of all electrons in the atom after its ionization and should generally give results closer to those experimentally obtained. In our calculations we used this general schema derived in [6, 13 and 8] in formulae. We omit magnetic and retardation terms and used formulae and program as described previously in [3]. Omitting magnetic and retardation terms is not important for all outer shells in the atom – if these terms are included, they change the eigenvalues less than 1% (as shown in the case of Hg [8]). For "method B" we have from [3] – TE (average total energy – "Hartree Type") or – AE (average energy – "Slater type") available, both defined previously in [3].

With the DFS method a similar set of integrodifferential Dirac-Hartree-Fock equations is solved as in [3] (see Eqs. (21 – 25) in [3]) but all terms representing different potentials from direct and exchange interaction of electrons (bound on different subshells) and containing $Y^E$, $Y_c^v$, $W_Q$ and $W_P$ in [3], are replaced by potential $V(r)$:

$$V(r) = -\frac{Z}{r} + \frac{1}{r} \int_0^r \varrho(s)\, ds + \int_r^\infty \frac{\varrho(s)}{s}\, ds + V_{ex}(r). \tag{1}$$

This potential term is the same for all electrons and contains radial electron density $\varrho$, the square value of the radial part of the Dirac wave function:

$$\varrho(r) = \sum_j [P_j^2(r) + Q_j^2(r)]. \tag{2}$$

In this DFS model the negatively charged electron density $\varrho$ interacts with the positively charged nucleus containing $Z$ protons. Electron density $\varrho$ is also interacting electrically with itself as expressed by the exchange potential $V_{ex}$:

$$V_{ex}(r) = -(C/r)\,[81\, r^n \varrho^m(r)/32\, \pi^2]^{\frac{1}{3}}. \tag{3}$$

Formula (3) was derived by Slater [9] with $C = 1$, $n = m = 1$. Gaspar [10] derived formula (3) with $C = 2/3$, $n = m = 1$ in a somewhat different way and Rosen and Lindgren [4] derived the modified DFS method (MDFS) by using formula (3) as a parametrical expression, when values $C$, $n$ and $m$ were obtained by variational DFS calculation, minimizing the total energy. In [4] the set of parameters $C$, $n$, $m$, was found giving minimal total energy [called parameters of optimized potential in (3)]. For heavy atoms the optimized potential $V_{ex}$ is

given with parameters $C \simeq 2/3$, $n = m = 1$, as in [10]. Because of the potential approximation (1), eigenvalues obtained by solving DFS integrodifferential equations do not exactly obey Koopman's theorem [7] as mentioned in [4]. The correct binding energies of subshell $i$, when calculated by "method A", are given in MDFS calculations [4]:

$$B_i = -\varepsilon_i - \delta\varepsilon_i \qquad (4)$$

where

$$\delta\varepsilon_i = \sum_j \langle ij|g|ij\rangle - \langle i|V(r) + Z/r|i\rangle \qquad (5)$$

is the term (see details in [4]) which corrects the inexact eigenvalue $\varepsilon_i$ to binding energy $B_i$. The first term (5) contains summations of Slater integrals $F^K$, $G^K$ with proper coefficients, similar to those described in Eq. (18) of the exact DHF method [3]. The difference is that here DFS wave functions (not exact) are used in place of exact DHF wave functions, when the Slater integrals $F^K$, $G^K$ or the second term in (5) are calculated. With correction (5) the MDFS method expresses total energy as [4]:

$$E_{\text{tot}} = \sum_i \varepsilon_i - \frac{1}{2}\sum_i \langle i|V(r) + Z/r|i\rangle + \frac{1}{2}\sum_i \delta\varepsilon_i. \qquad (6)$$

The normal DFS method (non modified) calculates $E_{\text{tot}}$ using (6), omitting the term $\frac{1}{2}\sum_i \delta\varepsilon_i$, which yields higher $E_{\text{tot}}$ values (with smaller absolute values) than the MDFS or DHF methods.

Generally, the MDFS method can be treated as some approximative DHF method: it calculates $E_{\text{tot}}$ with (6), i.e. using correct sums of Slater integrals $F^K$, $G^K$, but with wave functions self consistently calculated by DFS method using the same approximative potential $V(r)$ as defined in (1, 2, 3) when yielding non exact eigenvalues. We will see further that this approximation is the most valuable from DFS methods giving results close to DHF values.

When binding energies are calculated by DHF, MDFS or DFS method the total energy result corresponds to the barycentrum of the calculated electron configuration. Spectroscopically, this means that the calculated total energy should be compared with the barycentrum position of all terms included in a given electron configuration. The barycentrum position above ground term, $\Delta_{SP}$, is calculated according to the prescription in [11], p. 322, by the formula (for terms denoted in $LS$ coupling in non-relativistic classification):

$$\Delta_{SP} = \frac{\sum\limits_{L,S} \sum\limits_{J_{L,S}} (2J_{L,S} + 1) E(J_{L,S})}{\sum\limits_{L,S} \sum\limits_{J_{L,S}} (2J_{L,S} + 1)}. \qquad (7)$$

This formula means we take the energy $E(J_{L,S})$ of each term $(^{2S+1}L_J)$ (with $L$ denoted as $S$, $P$, $D$, $F$... symbol) with the statistical weight $(2J_{L,S} + 1)$ and sum all such contributions over all terms of the configuration. Here the factor $(2J_{L,S} + 1)$ is equal to the number of Zeeman lines, in which can split the multiplet

$^{2S+1}L$ having quantum number $J_{L,S}$ (it is equal to the number of separate wave functions of this multiplet).

In an exact comparison of DHF or DFS binding energies with experimental values, the experimental ionization potential (the difference of ground terms of atom and ion) must be corrected by $\Delta_{SP}$ of atom and ion.

For the inner subshells (corresponding to X-ray levels) the spin orbit interaction prevails and their binding energies calculated by method "A" or "B" can be compared directly with X-ray levels.

## 3. Results for Binding Energies

Results for ionization potential of several $1^+$ ions of Na, Mg, Al and systematically all $1^+$ ions of Th are presented in Table 1 and 2. In these tables total energies as $-TE$ or $-AE$ values were first calculated by the DHF method, as described in [3], each in the electronic configuration of ground state atom and $1^+$ ion (as shown in columns 1 and 2 of Tables 1 and 2). From the calculated values of $-TE$ and $-AE$ ("Hartree type" and "Slater type" total energies respectively) ionization potentials are calculated as DHF eigenvalues (marked "method A" in tables) and as the difference of $-TE$ or $-AE$ values of the atom and corresponding $1^+$ ion (marked "method B"). These values are compared with experimental X-ray levels in the last column. As experimental levels, values from [12] are used, corrected for work function ($+3.3$ eV for Th and standardly 4.4 eV for all other values, corresponding to the work function of Cu slit, see [12]).

Table 1. Ionization potentials of $1^+$ ions for Na, Mg, Al

| Atom or ion | Electron configuration | Total energy DHF calculated in AU; -TE or -AE values | $1^+$ ionized subshell | Ionization potential in AU from -TE or -AE values (method B) | Eigenvalues (AU) (method A) | Experimental X-ray level [12] AU |
|---|---|---|---|---|---|---|
| Na | (Ne) $3s^1 + = (Na^0)$ | 162.0783 | | | | |
| Na$^{1+}$ | (Na$^0$, $1s^1$ +) | 122.4329 | $1s$ + | 39.6454 (1.0016) | 40.54489 (1.0243) | 39.5827 |
| Na$^{1+}$ | (Na$^0$, $2s^1$ +) | 159.4309 | $2s$ + | 2.6474 (1.064) | 2.80541 (1.127) | 2.4893 |
| Na$^{1+}$ | (Na$^0$, $2p^1$ −) | 160.7286 | $2p$ − | 1.3497 (1.034) | 1.52204 (1.166) | 1.3053 |
| Na$^{1+}$ | (Na$^0$, $3s^1$ +) | 161.8961 | $3s$ + | 0.1822 (0.964) | 0.18234 (0.965) | 0.1890[a] |
| Mg | (Ne) $3s^2 + = (Mg^0)$ | 199.9353 | | | | |
| Mg$^{1+}$ | (Mg$^0$, $1s^1$ +) | 151.7404 | $1s$ + | 48.1949 (1.0010) | 49.12654 (1.0204) | 48.1464 |
| Mg$^{1+}$ | (Mg$^0$, $2s^1$ +) | 196.3418 | $2s$ + | 3.5935 (1.042) | 3.78017 (1.096) | 3.4490 |
| Mg$^{1+}$ | (Mg$^0$, $2p^1$ −) | 197.8544 | $2p$ − | 2.0809 (1.0124) | 2.28833 (1.113) | 2.0554 |
| Al | (Ne) $3s^2 + 3p^1 − = (Al^0)$ | 242.3315 | | | | |
| Al$^{1+}$ | (Al$^0$, $1s^1$ +) | 184.6739 | $1s$ + | 57.6576 (1.0026) | 58.63307 (1.0196) | 57.5080 |
| Al$^{1+}$ | (Al$^0$, $2s^1$ +) | 237.6271 | $2s$ + | 4.7044 (1.048) | 4.92893 (1.098) | 4.4896 |

[a] Optical data from [15].

Table 2. Ionization potentials of Th$^+$ ions

| Electron configuration | Total energy DHF calculated in AU | | 1$^+$ ionized subshell | Ionization potential from DHF values in AU (method B) | | Eigenvalues of (Th$^0$) AU (method A) AU | Experimental X-ray levels [12] AU |
|---|---|---|---|---|---|---|---|
| | $-$TE | $-$AE | | from $-$TE difference | from $-$AE difference | | |
| Th (Rn) $6d^2$ -- $7s^2$ + = Th$^0$ | 26525.270 | 26525.275 | | | | | |
| Th$^+$ (Th$^0$ with $1s^1$ +) | 22465.013 | 22465.019 | $1s$ + | 4060.257 | 4060.256 (1.0070) | 4064.0234 (1.0080) | 4031.968 ± 0.053 |
| Th$^+$ (Th$^0$ with $2s^1$ +) | 25768.073 | 25768.079 | $2s$ + | 757.197 | 757.196 (1.0057) | 759.4641 (1.0087) | 752.877 ± 0.038 |
| Th$^+$ (Th$^0$ with $2p^1$ −) | 25797.834 | 25797.840 | $2p$ − | 727.436 | 727.435 (1.0044) | 729.9306 (1.0079) | 724.237 ± 0.035 |
| Th$^+$ (Th$^0$ with $2p^3$ +) | 25924.217 | 25924.412 | $2p$ + | 601.053 | 600.863 (1.0023) | 603.5263 (1.0067) | 599.481 ± 0.031 |
| Th$^+$ (Th$^0$ with $3s^1$ +) | 26333.240 | 26333.246 | $3s$ + | 192.030 | 192.029 (1.0071) | 193.3199 (1.0138) | 190.674 ± 0.031 |
| Th$^+$ (Th$^0$ with $3p^1$ −) | 26346.474 | 26346.480 | $3p$ − | 178.796 | 178.795 (1.0060) | 180.1404 (1.0135) | 177.734 ± 0.035 |
| Th$^+$ (Th$^0$ with $3p^3$ +) | 26375.707 | 26375.783 | $3p$ + | 149.563 | 149.492 (1.0040) | 150.8630 (1.0132) | 148.896 ± 0.035 |
| Th$^+$ (Th$^0$ with $3d^3$ −) | 26396.441 | 26396.530 | $3d$ − | 128.829 | 128.745 (1.0021) | 130.2806 (1.0140) | 128.478 ± 0.031 |
| Th$^+$ (Th$^0$ with $3d^5$ +) | 26402.356 | 26402.440 | $3d$ + | 122.914 | 122.835 (1.0016) | 124.3223 (1.0137) | 122.639 ± 0.031 |
| Th$^+$ (Th$^0$ with $4s^1$ +) | 26475.619 | 26475.625 | $4s$ + | 49.651 | 49.650 (1.0131) | 50.2470 (1.0253) | 49.007 ± 0.035 |
| Th$^+$ (Th$^0$ with $4p^1$ −) | 26481.529 | 26481.535 | $4p$ − | 43.741 | 43.740 (1.0154) | 44.3480 (1.0295) | 43.076 ± 0.035 |
| Th$^+$ (Th$^0$ with $4p^3$ +) | 26489.150 | 26489.188 | $4p$ + | 36.120 | 36.087 (1.0112) | 36.6981 (1.0283) | 35.689 ± 0.035 |
| Th$^+$ (Th$^0$ with $4d^3$ −) | 26498.545 | 26498.583 | $4d$ − | 26.725 | 26.692 (1.0119) | 27.3098 (1.0353) | 26.379 ± 0.035 |
| Th$^+$ (Th$^0$ with $4d^5$ +) | 26499.964 | 26500.000 | $4d$ + | 25.306 | 25.275 (1.0112) | 25.8787 (1.0354) | 24.993 ± 0.035 |
| Th$^+$ (Th$^0$ with $4f^5$ −) | 26512.337 | 26512.374 | $4f$ − | 12.933 | 12.901 (1.0091) | 13.5140 (1.0570) | 12.785 ± 0.031 |
| Th$^+$ (Th$^0$ with $4f^7$ +) | 26512.689 | 26512.722 | $4f$ + | 12.581 | 12.553 (1.0085) | 13.1536 (1.0568) | 12.447 ± 0.035 |
| Th$^+$ (Th$^0$ with $5s^1$ +) | 26513.941 | 26513.947 | $5s$ + | 11.329 | 11.328 (1.0497) | 11.5739 (1.0724) | 10.792 ± 0.050 |
| Th$^+$ (Th$^0$ with $5p^1$ −) | 26516.265 | 26516.271 | $5p$ − | 9.005 | 9.004 (1.0524) | 9.24579 (1.0794) | 8.556 ± 0.060 |
| Th$^+$ (Th$^0$ with $5p^3$ +) | 26518.016 | 26518.037 | $5p$ + | 7.254 | 7.238 (1.0635) | 7.49209 (1.1008) | 6.806 ± 0.035 |
| Th$^+$ (Th$^0$ with $5d^3$ −) | 26521.511 | 26521.530 | $5d$ − | 3.759 | 3.745 (1.0435) | 3.97292 (1.1070) | 3.589 ± 0.035 |
| Th$^+$ (Th$^0$ with $5d^5$ +) | 26521.773 | 26521.792 | $5d$ + | 3.497 | 3.483 (1.0388) | 3.70088 (1.1038) | 3.353 ± 0.035 |
| Th$^+$ (Th$^0$ with $6s^1$ +) | 26523.295 | 26523.301 | $6s$ + | 1.975 | 1.974 (0.8549) | 2.05992 (0.8921) | 2.309 ± 0.06 |
| Th$^+$ (Th$^0$ with $6p^1$ −) | 26524.021 | 26524.027 | $6p$ − | 1.249 | 1.248 (0.6490) | 1.32886 (0.7910) | 1.923 ± 0.12 |
| Th$^+$ (Th$^0$ with $6p^3$ +) | 26524.369 | 26524.382 | $6p$ + | 0.901 | 0.893 (0.5248) | 0.98138 (0.5766) | 1.702 ± 0.12 |
| Th$^+$ (Th$^0$ with $6d^1$ −) | 26525.070 | 26525.074 | $6d$ − | 0.200 | 0.201 (1.0308) | 0.22875 (1.1730) | 0.195 ± 0.15 [18] |
| Th$^+$ (Th$^0$ with $7s^1$ +) | 26525.075 | 26525.081 | $7s$ + | 0.195 | 0.194 (0.7578) | 0.20651 (0.8067) | 0.256 ± 0.15 [16] |
| | | | | | | | 0.276 ± 0.15 [17] |

The ratio of DHF calculated values to experimental X-ray levels is indicated in parentheses, showing the exactness of calculations. From these tables it is visible that ionization potential calculated by "method B" agree better with the experiment than potentials calculated by "method A". "Method B" values for $1s+$ shell in the cases Na, Mg, Al are most exact (no relativistic effect is visible on this shell for lower $Z$), differing only $0.1 - 0.26\%$ from the experiment, with all other values less exact, but still differing only $3 - 6\%$ from the experiment. In the case of Th by "method B" error on $1s+$ and $2s+$ values is 0.7% (due to the point nucleus approximation) and drops to 0.23% on the $2p+$ values. On all levels with main quantum numbers 3 and 4, agreement is very good for levels 3 (giving errors from $0.71 - 0.16\%$) and good for levels 4 (within $\sim 1\%$). Agreement is not very good for levels 5, 6 and 7. "Method A" is systematically giving somewhat higher results than "method B". However for the last shells ($3s+$ in Na or 6th and 7th in Th) our results from "A" are closer to experiments than from "B".

In the case of Th one can observe systematics in the deviations between experiments and "method B" results. Shells with 2 electrons ($s+$ or $p-$) show the greatest deviation. As the number of electrons on closed shells increases, the difference decreases from $3s+$ to $3d+$ or from $4s+$ to $4f+$.

Table 3. Comparison of calculated values for $Hg^{80}$ (AU)

| $1^+$ Ionized subshell | Binding energies Eigenvalues DHF This work (method A) | MDFS [4] (method A) | MDFS [4] (method B) | Correction [8] $\Delta_{G+R}$ | Binding energies Expected values (MDFS $-\Delta_{G+R}$) | Experimental values [12] |
|---|---|---|---|---|---|---|
| $1s+$ | 3076.1399 | 3076.15 | 3072.70 (1.0061) | −11.374 | 3061.33 (1.00234) | 3054.19 ± 0.030 |
| $2s+$ | 550.5322 | 550.50 | 548.41 (1.0053) | −1.548 | 546.86 (1.00247) | 545.51 ± 0.035 |
| $2p-$ | 526.8543 | 526.85 | 524.55 (1.0042) | −2.407 | 522.14 (0.99962) | 522.34 ± 0.025 |
| $2p+$ | 455.1315 | 455.13 | 453.04 (1.0042) | −1.542 | 451.50 (0.99978) | 451.60 ± 0.015 |
| $3s+$ | 133.1796 | 133.14 | 131.90 (1.0064) | −0.358 | 131.54 (1.00366) | 131.06 ± 0.040 |
| $3p-$ | 122.6415 | 122.61 | 121.32 (1.0056) | −0.503 | 120.82 (1.00141) | 120.65 ± 0.045 |
| $3p+$ | 106.5334 | 106.52 | | −0.336 | | 104.80 ± 0.015 |
| $3d-$ | 89.4262 | 89.41 | 88.15 (1.0039) | −0.306 | 87.84 (1.00034) | 87.81 ± 0.010 |
| $3d+$ | 86.0061 | 86.00 | | −0.239 | | 84.50 ± 0.010 |
| $4s+$ | 30.6701 | 30.66 | 30.04 (1.0156) | −0.093 | 29.95 (1.0125) | 29.58 ± 0.035 |
| $4p-$ | 26.1297 | 26.12 | 25.50 (1.0185) | −0.130 | 25.37 (1.0132) | 25.04 ± 0.085 |
| $4p+$ | 22.1865 | 22.19 | | −0.080 | | 21.15 ± 0.050 |
| $4d-$ | 14.7954 | 14.80 | 14.27 (1.0142) | −0.064 | 14.21 (1.0099) | 14.07 ± 0.035 |
| $4d+$ | 14.0473 | 14.05 | | −0.049 | | 13.38 ± 0.045 |
| $4f-$ | 4.4644 | 4.476 | 3.999 (1.0176) | −0.028 | 3.971 (1.0104) | 3.93 ± 0.020 |
| $4f+$ | 4.3025 | 4.315 | | −0.022 | | 3.79 ± 0.020 |
| $5s+$ | 5.1088 | 5.125 | 4.896 (1.0667) | −0.018 | 4.878 (1.0627) | 4.59 ± 0.045 |
| $5p-$ | 3.5402 | 3.553 | 3.344 (1.0718) | −0.022 | 3.322 (1.0647) | 3.12 ± 0.045 |
| $5p+$ | 2.8418 | 2.856 | 2.687 (1.1785) | −0.013 | 2.674 (1.1728) | 2.28 ± 0.045 |
| $5d-$ | 0.65009 | 0.659 | 0.543 (0.884) | −0.006 | 0.537 (0.875) | 0.614 ± 0.050[a] |
| $5d+$ | 0.57382 | 0.584 | 0.483 (0.886) | −0.004 | 0.479 (0.879) | 0.545 ± 0.050[a] |
| $6s+$ | 0.32863 | 0.340 | 0.312 (0.813) | −0.002 | 0.310 (0.813) | 0.384 ± 0.050[a] |

[a] Data from optical system of [14].

The explanation for this behaviour could be connected with the fact that magnetic and retardation terms are omitted in formulae [3].

We may demonstrate this in the case of $Hg^{80}$, calculated exactly in [8] ("method A") with all magnetic and retardation terms included. In Table 3 we compared our results by "method A" for $Hg^{80}$ (column 1) with MDFS corrected binding energies obtained by methods "A" and "B" from paper [4] with optimized potential – using formula (5) for "A" and the difference of atom and ion total energies from "B", as defined in formula (6).

Our results from "method A" and [4] show excellent agreement, proving that MDFS results of (4) are essentially very close to our DHF results. The ratio of "method B" results in Table 3 to experimental values, as presented in parentheses, show similarity to equivalent ratios in the case of our Th + calculations (see Table 2, "method B"). We also compared our DHF values – eigenvalues for Cu, Kr, J, Eu and U from [3] with binding energies of "method A" calculated in [4] using Eqs. (1–6). The agreement with our DHF eigenvalues was also very good in all levels of these cases (from $Z = 29$ to $Z = 92$), as in the case of $Hg^{80}$ in Table 3. From this we can confirm the conclusion drawn in [4] that the MDFS method gives (up to $Z = 92$) practically the same results as DHF. Furthermore, if we use (in Table 3) the sum of magnetic (Gaunt) and retardation terms calculated exactly for $Hg^{80}$ in [8] as correction $\Delta_{G+R}$ (Table 3, column 6), which lowers the binding energies "B", we may obtain the expected experimental values (column 6). When we compare the expected values with experimental values (its ratio in parentheses, sixth column) we see agreement is greatly

Table 4. Ionization potential of polyvalent ions

| Ionization process | Electron structure of ion in ground state (DHF) | Calculated ionization potential (DHF) in AU in AU | | | Experimental ionization potential (AU) [15] | |
|---|---|---|---|---|---|---|
| | | From -TE difference | From -AE difference | From eigen-values | Directly measured | Barycentrum difference |
| Na → Na$^{1+}$ | (Ne) | 0.1822 | 0.1822 (0.964) | 0.18234 (0.965) | 0.1890 | 0.1890 (0.965)[a] |
| Mg → Mg$^{2+}$ | (Ne) | 0.7850 | 0.7850 (0.941) | | 0.8340 | 0.8340 |
| Al → Al$^{3+}$ | (Ne) | 1.8794 | 1.8794 (0.960) | | 1.9584 | 1.9581 |
| Si → Si$^{1+}$ | (Ne) $3s^2 + 3p^1$ – | 0.2486 | 0.2486 (0.829) | 0.26695 (0.891) | 0.2997 | 0.2859 (0.934) |
| Si → Si$^{2+}$ | (Ne) $3s^2$ + | 0.8263 | 0.8263 (0.917) | 0.85339 (0.947) | 0.9007 | 0.8860 (0.963) |
| Si → Si$^{3+}$ | (Ne) $3s^1$ + | 2.0032 | 2.0032 (0.939) | 2.03784 (0.956) | 2.1322 | 2.1175 (0.962) |
| Si → Si$^{4+}$ | (Ne) | 3.6472 | 3.6472 (0.962) | 3.68269 (0.971) | 3.7920 | 3.7773 (0.975) |
| Th → Th$^{1+}$ | (Rn) $6d^2 - 7s^1$ + | 0.195 | 0.194 (0.758) | 0.20651 (0.807) | 0.256 [16] 0.276 [17] | |
| Th → Th$^{2+}$ | (Rn) $6d^2$ – | 0.602 | 0.601 (0.860) | 0.61602 (0.881) | 0.699 [15] | |
| Th → Th$^{3+}$ | (Rn) $5f^1$ – | 1.253 | 1.251 (0.872) | 1.27782 (0.891) | 1.434 [15] | |
| Th → Th$^{4+}$ | (Rn) | 2.232 | 2.237 (0.897) | 2.31642 (0.929) | 2.493 [15] | |

[a] In the last column are ratio: $\dfrac{\text{IP from eigenvalues}}{\text{IP from barycentrum difference}}$ ; other values are compared to IP directly measured.

improved. With the exclusion of ionization levels $1s+$ and $2s+$ (deviation caused by point nucleus approximation and Lamb shift) the expected binding energies agree almost exactly with the experiment for the main quantum levels 2, 3 and 4. However, even after deducing $\Delta_{G+R}$, one can see that for quantum levels 5 and 6, agreement is not very good with data from X-ray or optical spectra. This is equally valid for more exact DHF calculations of Hg eigenvalues [8] which includes the magnetic and retardation terms and finite nucleus.

The remaining difference (after deducing $\Delta_{G+R}$) is, perhaps, caused by correlation effects and by approximations used in Dirac-Hartree-Fock Eqs. in [3] or [8] – e.g. by using the nonexact $\Gamma_{ikj}$ coefficient for open shells, which is valid exactly for an atom with only all closed shells. It is apparent that calculation of the $1^+$ ionized shell (by "method B") from a subshell with many electrons (as $nd+$ or $nf+$ shell) is more exact than calculation of the $1^+$ ion from $s+$ or $p-$ subshells (containing only 2 electrons when the shell is full) – when the same $\Gamma_{ikj}$ coefficients valid for closed shells are used (see inner subshells in Table 3 with $\Delta_{G+R}$ correction, or in Table 2 without such correction).

In Table 4, similar calculations for $1^+$, $2^+$, $3^+$, $4^+$ ions are shown as in Tables 1, 2, 3 for $1^+$ ions.

In DHF calculations it is visible that in all cases the accord is better in the region of valence electrons with eigenvalues, obtained from "method A", than with values obtained by "method B".

This accord can be somewhat improved when DHF results are compared with ionization potentials obtained from the barycentrum difference using calculations $\Delta_{SP}$ from formula (7) for atom and ion (see Table 4, last column).

Generally, Tables 1, 2, 3, 4 show the accuracy with which ionization potentials from DHF values can be calculated, using approximations as described in [3]. It is visible that accuracy of $0.1-2\%$ can be achieved in comparison to X-ray levels, for all inner shells when the deviation of eigenvalues from experimental ionization potentials for valence electrons is in the range $2-10\%$.

## 4. Results for the First Ionization Potentials

The preceding tables have shown that the first ionization potentials for valence electrons closest to experimental values can be found most simply from DHF eigenvalues with an accuracy of $\sim 10\%$. Therefore we use our eigenvalues from data calculated in [3] to compare first ionization potentials of all atoms in the periodic system with their experimental values (in $Z = 1-88$ region, see Table 5). In a previous paper [3], we found some discrepancies between DHF calculated and measured ground state electron configurations in cases Cr, Cu, Nb, Te and Pd. However, these discrepancies could be only apparent and need to be verified by the exact calculations of barycentrum positions of both concurrent electron states, according to (7), including the statistically weighted participation of $(+)$ and $(-)$ states in each open $n, l$ subshell.

At present, therefore, we compare both possible configurations in Table 5. The ratios of the first ionization potential calculated by DHF to the experimental

Table 5. First ionization potential in the periodic system

| Element | $Z$ | Ionized level | Ionization potential (eV) | | | I.P. from barycentrum difference | Barycentrum correlation ratio |
|---|---|---|---|---|---|---|---|
| | | | Calculated DHF I.P. | Experimental I.P. [15] | Correlation ratio | | |
| H | 1 | $1s^1 +$ | 13.598 | 13.598 | 1.000 | 13.598 | 1.000 |
| He | 2 | $1s^2 +$ | 24.966 | 24.587 | 1.015 | 24.587 | 1.015 |
| Li | 3 | $1s^1 +$ | 5.340 | 5.392 | 0.990 | 5.392 | 0.990 |
| | | $1s^2 +$ | 67.392 | | | | |
| Be | 4 | $2s^2 +$ | 8.412 | 9.322 | 0.902 | 9.322 | 0.902 |
| | | $1s^2 +$ | 128.733 | | | | |
| B | 5 | $2p^1 -$ | 8.426 | 8.298 | 1.016 | 8.297 | 1.016 |
| | | $2s^2 +$ | 13.459 | | | | |
| C | 6 | $2p^2 -$ | 10.599 | 11.260 | 0.941 | 10.710 | 0.990 |
| | | $2s^2 +$ | 19.496 | | | | |
| N | 7 | $2p^2 -$ | 13.323 | 14.534 | 0.917 | 13.220 | 1.008 |
| | | $2p^1 +$ | 14.673 | | | | |
| O | 8 | $2p^2 -$ | 16.326 | 13.618 | 1.200 | 15.911 | 1.026 |
| | | $2p^2 +$ | 17.327 | | | | |
| F | 9 | $2p^2 -$ | 19.614 | 17.422 | 1.126 | 18.652 | 1.052 |
| | | $2p^3 +$ | 20.124 | | | | |
| Ne | 10 | $2p^4 +$ | 23.069 | 21.564 | 1.070 | 21.564 | 1.070 |
| | | $2p^2 -$ | 23.194 | | | | |
| Na | 11 | $3s^1 +$ | 4.959 | 5.139 | 0.965 | 5.139 | 0.965 |
| | | $2p^4 +$ | 41.191 | | | | |
| Mg | 12 | $3s^2 +$ | 6.893 | 7.646 | 0.902 | 7.646 | 0.902 |
| | | $2p^4 +$ | 61.917 | | | | |
| Al | 13 | $3p^1 -$ | 5.711 | 5.986 | 0.954 | 5.977 | 0.955 |
| | | $3s^2 +$ | 10.722 | | | | |
| Si | 14 | $3p^2 -$ | 7.260 | 8.151 | 0.891 | 7.777 | 0.934 |
| | | $3s^2 +$ | 14.891 | | | | |
| P | 15 | $3p^2 -$ | 9.225 | 10.486 | 0.880 | 9.654 | 0.956 |
| | | $3p^1 +$ | 10.016 | | | | |
| S | 16 | $3p^2 -$ | 11.366 | 10.360 | 1.097 | 11.615 | 0.979 |
| | | $3p^2 +$ | 11.907 | | | | |
| Cl | 17 | $3p^2 -$ | 13.688 | 12.967 | 1.056 | 13.668 | 1.001 |
| | | $3p^3 +$ | 13.895 | | | | |
| Ar | 18 | $3p^4 +$ | 15.986 | 15.759 | 1.014 | 15.759 | 1.014 |
| | | $3p^2 -$ | 16.194 | | | | |
| K | 19 | $4s^1 +$ | 4.026 | 4.341 | 0.927 | | |
| | | $3p^4 +$ | 25.823 | | | | |
| Ca | 20 | $4s^2 +$ | 5.339 | 6.113 | 0.874 | | |
| | | $3p^4 +$ | 36.272 | | | | |
| Sc | 21 | $4s^2 +$ | 5.740 | 6.54 | 0.878 | | |
| | | $3d^1 -$ | 9.512 | | | | |
| Ti | 22 | $4s^2 +$ | 6.068 | 6.82 | 0.890 | | |
| | | $3d^2 -$ | 11.177 | | | | |
| V | 23 | $4s^2 +$ | 6.363 | 6.74 | 0.945 | | |
| | | $3d^3 -$ | 12.655 | | | | |
| Cr | 24[a] | $4s^2 +$ | 6.638 | 6.766 | 0.980 | | |
| | | $3d^4 -$ | 14.023 | | | | |
| Cr | 24[b] | $4s^1 +$ | 5.708 | 6.766 | 0.844 | | |
| | | $3d^1 +$ | 8.532 | | | | |
| Mn | 25 | $4s^2 +$ | 6.904 | 7.435 | 0.930 | | |
| | | $3d^1 +$ | 14.904 | | | | |
| Fe | 26 | $4s^2 +$ | 7.159 | 7.870 | 0.910 | | |
| | | $3d^2 +$ | 16.105 | | | | |

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Table 5 (continued)

| Element | Z | Ionized level | Ionization potential (eV) | | |
|---|---|---|---|---|---|
| | | | Calculated DHF I.P. | Experimental I.P. [15] | Correlation ratio |
| Co | 27 | $4s^2 +$ | 7.408 | 7.86 | 0.943 |
| | | $3d^3 +$ | 17.261 | | |
| Ni | 28 | $4s^2 +$ | 7.650 | 7.635 | 1.002 |
| | | $3d^4 +$ | 18.378 | | |
| Cu | 29[a] | $4s^2 +$ | 7.888 | 7.726 | 1.020 |
| | | $3d^5 +$ | 19.464 | | |
| Cu | 29[b] | $4s^1 +$ | 6.657 | 7.726 | 0.861 |
| | | $3d^6 +$ | 12.898 | | |
| Zn | 30 | $4s^2 +$ | 8.122 | 9.394 | 0.864 |
| | | $3d^6 +$ | 20.524 | | |
| Ga | 31 | $4p^1 -$ | 5.707 | 5.999 | 0.952 |
| | | $4s^2 +$ | 11.773 | | |
| Ge | 32 | $4p^2 -$ | 7.060 | 7.899 | 0.894 |
| | | $4s^2 +$ | 15.505 | | |
| As | 33 | $4p^2 -$ | 8.800 | 9.81 | 0.898 |
| | | $4p^1 +$ | 9.268 | | |
| Se | 34 | $4p^2 -$ | 10.654 | 9.752 | 1.093 |
| | | $4p^2 +$ | 10.789 | | |
| Br | 35 | $4p^3 +$ | 12.360 | 11.814 | 1.045 |
| | | $4p^2 -$ | 12.360 | | |
| Kr | 36 | $4p^4 +$ | 13.987 | 13.999 | 0.999 |
| | | $4p^2 -$ | 14.731 | | |
| Rb | 37 | $5s^1 +$ | 3.809 | 4.177 | 0.911 |
| | | $4p^4 +$ | 21.653 | | |
| Sr | 38 | $5s^2 +$ | 4.930 | 5.695 | 0.866 |
| | | $4p^4 +$ | 29.366 | | |
| Y | 39 | $5s^2 +$ | 5.457 | 6.38 | 0.855 |
| | | $4d^1 -$ | 6.599 | | |
| Zr | 40 | $5s^2 +$ | 5.830 | 6.84 | 0.853 |
| | | $4d^2 -$ | 8.230 | | |
| Nb | 41[a] | $5s^2 +$ | 6.135 | 6.88 | 0.891 |
| | | $4d^3 -$ | 9.752 | | |
| Nb | 41[b] | $5s^1 +$ | 5.538 | 6.88 | 0.805 |
| | | $4d^4 -$ | 7.165 | | |
| Mo | 42[a] | $5s^2 +$ | 6.401 | 7.099 | 0.902 |
| | | $4d^4 -$ | 11.229 | | |
| Mo | 42[b] | $5s^1 +$ | 5.727 | 7.099 | 0.808 |
| | | $4d^1 +$ | 7.954 | | |
| Tc | 43[a] | $5s^1 +$ | 5.895 | 7.28 | 0.811 |
| | | $4d^2 +$ | 9.087 | | |
| Tc | 43[b] | $5s^2 +$ | 6.648 | 7.28 | 0.912 |
| | | $4d^1 +$ | 12.213 | | |
| Ru | 44 | $5s^1 +$ | 6.049 | 7.37 | 0.821 |
| | | $4d^3 +$ | 10.216 | | |
| Rh | 45 | $5s^1 +$ | 6.191 | 7.46 | 0.831 |
| | | $4d^4 +$ | 11.347 | | |
| Pd | 46[a] | $5s^1 +$ | 6.325 | 8.34 | 0.758 |
| | | $5d^5 +$ | 12.486 | | |
| | 46[b] | $4d^6 +$ | 8.694 | 8.34 | 1.041 |
| | | $4d^4 -$ | 9.266 | | |
| Ag | 47 | $5s^1 +$ | 6.452 | 7.576 | 0.852 |
| | | $4d^6 +$ | 13.633 | | |

Table 5 (continued)

| Element | Z | Ionized level | Ionization potential (eV) | | |
|---|---|---|---|---|---|
| | | | Calculated DHF I.P. | Experimental I.P. [15] | Correlation ratio |
| Cd | 48 | $5s^2 +$ | 7.657 | 8.993 | 0.852 |
| | | $4d^6 +$ | 19.270 | | |
| In | 49 | $5p^1 -$ | 5.492 | 5.786 | 0.949 |
| | | $5s^2 +$ | 10.699 | | |
| Sn | 50 | $5p^2 -$ | 6.631 | 7.344 | 0.892 |
| | | $5s^2 +$ | 13.762 | | |
| Sb | 51 | $5p^1 +$ | 8.147 | 8.641 | 0.943 |
| | | $5p^2 -$ | 8.197 | | |
| Te | 52 | $5p^2 +$ | 9.392 | 9.009 | 1.043 |
| | | $5p^2 -$ | 9.843 | | |
| I | 53 | $5p^3 +$ | 10.660 | 10.451 | 0.981 |
| | | $5p^2 -$ | 11.576 | | |
| Xe | 54 | $5p^4 +$ | 11.958 | 12.130 | 0.985 |
| | | $5p^2 +$ | 13.403 | | |
| Cs | 55 | $6s^1 +$ | 3.488 | 3.894 | 0.897 |
| | | $5p^4 +$ | 17.928 | | |
| Ba | 56 | $6s^2 +$ | 4.439 | 5.212 | 0.852 |
| | | $5p^4 +$ | 23.728 | | |
| La | 57 | $6s^2 +$ | 4.867 | 5.577 | 0.873 |
| | | $5d^1 -$ | 6.724 | | |
| Hf | 72 | $6s^2 +$ | 6.440 | 7.0 | 0.920 |
| | | $5d^2 -$ | 6.953 | | |
| Ta | 73 | $6s^2 +$ | 6.807 | 7.89 | 0.863 |
| | | $5d^3 -$ | 8.270 | | |
| W | 74 | $6s^2 +$ | 7.134 | 7.98 | 0.894 |
| | | $5d^4 -$ | 9.536 | | |
| Re | 75 | $6s^2 +$ | 7.477 | 7.88 | 0.948 |
| | | $5d^1 +$ | 9.704 | | |
| Os | 76 | $6s^2 +$ | 7.794 | 8.7 | 0.896 |
| | | $5d^2 +$ | 10.885 | | |
| Ir | 77 | $6s^2 +$ | 8.095 | 9.1 | 0.890 |
| | | $5d^3 +$ | 12.061 | | |
| Pt | 78[a] | $6s^1 +$ | 7.722 | 9.0 | 0.859 |
| | | $5d^5 +$ | 10.642 | | |
| Pt | 78[b] | $6s^2 +$ | 8.384 | 9.0 | 0.932 |
| | | $5d^4 +$ | 13.238 | | |
| Au | 79 | $6s^1 +$ | 7.948 | 9.225 | 0.859 |
| | | $5d^6 +$ | 11.647 | | |
| Hg | 80 | $6s^2 +$ | 8.937 | 10.437 | 0.857 |
| | | $5d^6 +$ | 15.606 | | |
| Tl | 81 | $6p^1 -$ | 5.805 | 6.108 | 0.948 |
| | | $6s^2 +$ | 11.921 | | |
| Pb | 82 | $6p^2 -$ | 6.904 | 7.416 | 0.932 |
| | | $6s^2 +$ | 14.907 | | |
| Bi | 83 | $6p^1 +$ | 6.995 | 7.286 | 0.962 |
| | | $6p^2 -$ | 8.754 | | |
| Po | 84 | $6p^2 +$ | 8.142 | 8.42 | 0.968 |
| | | $6p^2 -$ | 10.656 | | |
| At | 85 | $6p^3 +$ | 9.286 | | $(0.969)^c$ |
| | | $6p^2 -$ | 12.638 | | |
| Rn | 86 | $6p^4 +$ | 10.438 | 10.748 | 0.970 |
| | | $6p^2 -$ | 14.709 | | |

Table 5 (continued)

| Element | Z | Ionized level | Ionization potential (eV) | | |
|---------|---|---------------|---------------------------|---|---|
| | | | Calculated DHF I.P. | Experimental I.P. [15] | Correlation ratio |
| Fr | 87 | $7s^1 +$ | 3.614 | | $(0.914)^c$ |
| | | $6p^4 +$ | 15.402 | | |
| Ra | 88 | $7s^2 +$ | 4.527 | 5.279 | 0.858 |
| | | $6p^4 +$ | 20.126 | | |
| Ac | 89 | $6d^1 -$ | 5.100 | | |
| | | $7s^2 +$ | 5.139 | | |

[a, b] Corresponds to two possible ground states (see [3]).
[c] Interpolated values.

one (called correlation ratio) are presented in column 5. For comparison we present the ionization potential for the $1^+$ ion of the two lowest lying subshells in each atom. From this one can see how both subshells are energetically close. Some $p-$ and $p+$ subshells, when both are full or close to be full, are really energetically very close, as visible in Table 5.

The agreement of experimental and calculated values is good, usually within $\sim 10\%$. For the first two periods (up to Ar) we also calculated ionization potentials for the barycentrum position of spectral lines of atom and ion, according to formula (7) using data of [15]. The agreement is substantially improved in some cases (see "barycentrum correlation ratio" when the difference of the ion and atom barycentrum is used as the experimental ionization potential). However, this comparison is not completly valid, because we correlate DHF values which were calculated for a full $2p-$ or $3p-$ shell and a non-filled $2p+$ or $3p+$ shell – with spectroscopic barycentrum difference, which contains the statistically weighted spectroscopic terms from a non-relativistic $2p$ or $3p$ shell according to (7) $(LS$ coupling). This correlation supposes that $p-$ and $p+$ shells have the same ionization potential which is only a crude approximation here. For correct correlation more DHF calculations are needed. For example DHF values calculated for $(2p^1 - 2p^3 +)$, $(2p^4 +)$, $(2p^2 - 2p^2 +)$ states in the case of oxygen (calculated in $jj$ coupling) should be statically weighted similarly as in (7) to obtain the average energy of the $(2p^4)$ oxygen state, using more complex formulae, see e.g. [22].

It is interesting to observe that correlation ratios have a systematic "periodic behavior", moving from the beginning to the end of each period, as visible from Fig. 1. From this figure one can make a fairly reasonable extrapolation along the $Z$ axis for each chemical group of the periodic system to the region of $104-120$ elements. In Fig. 1 it is visible that all $s$ and $p$ elements are forming a curve in each period with a maximum on the 6th group (O, S, Se, Tc, Po). Good extrapolation for all $s$ and $p$ elements can be made by linear extension of their correlation ratios between the last two members of each chemical group. By this way extrapolation ratios were obtained for $112-120$ element. As another possible extrapolation method for element 116, linear interpolation between
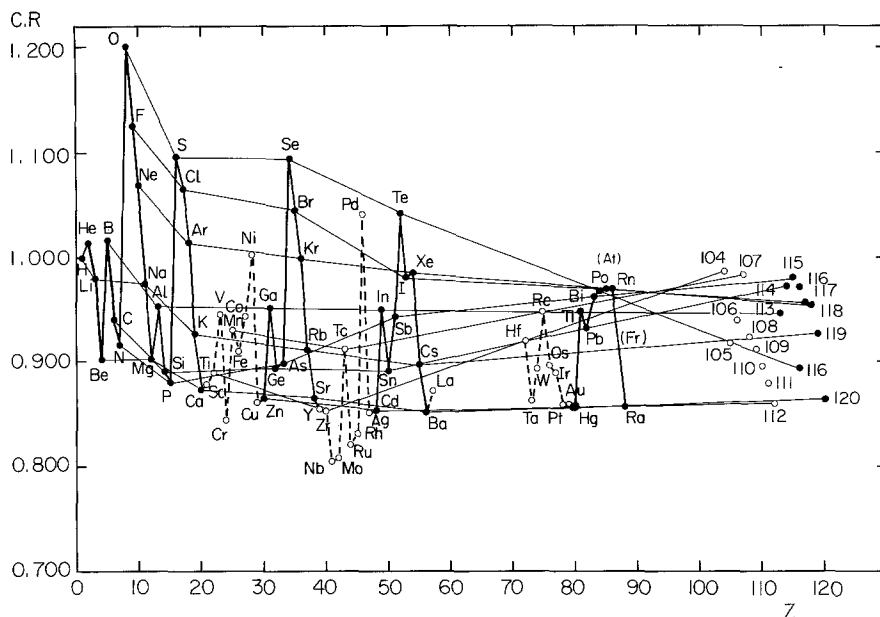
Fig. 1. Correlation ratios in the periodic system. ● s and p elements; ○ d elements. Values for 104, 107, 112 − 120 elements are linearly extrapolated correlation ratios. Values for 105, 106, 108 and 109 element are extrapolated with aid of Fig. 2. Points for 110, 111 element in Fig. 1 are interpolated between values for 109 and 112 element
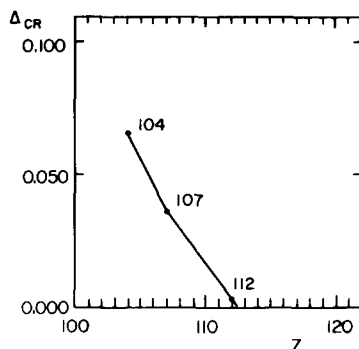


Fig. 2. Correction of correlation ratios for d elements $\Delta_{CR}$ in the 104 − 112 element region

extrapolated values of 118 and 115 elements was used. To obtain values for elements 117 and 119, the interpolation between Ra and Rn and Po was used first, to obtain correlation ratios for At and Fr as a basis for extrapolation. For d elements direct extrapolation is possible for 104, 107 and 112 elements − they have systematically similar electron structure ($xds^2$). For 105, 108, 109, 110 and 111 elements such extrapolation is impossible because their chemical analogues in the periodic system either do not have an electron structure analogical to them (Pt, Au) or do not have analogical electron structure just before and after the

Table 6. First ionization potential for $Z = 104 - 120$ elements

| Element $Z$ | Ionized level | Ionization potential (eV) | | | Expected I.P | |
|---|---|---|---|---|---|---|
| | | Calculated DHF I.P. | Expected I.P. | Extra-polated correlation ratio | From DFS data [1] | Extrapolated from periodic system [20, 19] |
| 104[a] | $7p^1-$ | 5.049 | 5.1 | | | |
| | $6d^1-$ | 8.070 | | | | |
| 104[b] | $6d^2-$ | 5.770 | 5.9 | 0.986 | 5.1 | |
| | $7s^2+$ | 7.290 | | | | |
| 105[a] | $6d^3-$ | 6.871 | 7.5 | 0.918 | 6.2 | |
| | $7s^2+$ | 7.874 | | | | |
| 105[b] | $7p^1-$ | 5.518 | 6.0 | | | |
| | $6d^2-$ | 9.252 | | | | |
| 106 | $6d^4-$ | 7.906 | 8.4 | 0.939 | 7.1 | |
| | $7s^2+$ | 8.408 | | | | |
| 107 | $6d^1+$ | 7.289 | 7.4 | 0.983 | 6.5 | |
| | $7s^2+$ | 9.084 | | | | |
| 108 | $6d^2+$ | 8.242 | 8.9 | 0.924 | 7.4 | |
| | $7s^2+$ | 9.751 | | | | |
| 109 | $6d^3+$ | 9.173 | 10.1 | 0.912 | 8.2 | |
| | $7s^2+$ | 10.421 | | | | |
| 110 | $6d^4+$ | 10.093 | 11.3 | 0.895 | 9.4 | |
| | $7s^2+$ | 11.106 | | | | |
| 111 | $6d^5+$ | 11.005 | 12.5 | 0.880 | 10.3 | |
| | $7s^2+$ | 11.811 | | | | |
| 112 | $6d^6+$ | 11.918 | 13.9 | 0.860 | 11.2 | |
| | $7s^2+$ | 12.549 | | | | |
| 113 | $7p^1-$ | 7.464 | 7.9 | 0.946 | 7.5, 7.4 [21] | 5.98 [20] |
| | $6d^6+$ | 15.325 | | | | |
| 114 | $7p^2-$ | 8.519 | 8.8 | 0.972 | 8.5, 8.5 [21] | |
| | $7s^2+$ | 18.455 | | | | |
| 115 | $7p^1+$ | 5.046 | 5.1 | 0.981 | 5.9 | |
| | $7p^2-$ | 11.491 | | | | |
| 116 | $7p^2+$ | 6.170 | 6.6 | 0.933 | 6.8 | |
| | $7p^2-$ | 14.344 | | | | |
| 117 | $7p^3+$ | 7.220 | 7.6 | 0.957 | 8.2 | 8.41 [20] 9.3 [19] |
| | $7p^2-$ | 17.264 | | | | |
| 118 | $7p^4+$ | 8.243 | 8.6 | 0.955 | 9.0 | 9.8 [19] |
| | $7p^2-$ | 20.309 | | | | |
| 119 | $8s^1+$ | 4.454 | 4.9 | 0.916 | 4.1 | 3.72 [20] 3.6 [19] |
| | $7p^4+$ | 11.661 | | | | |
| 120 | $8s^2+$ | 5.368 | 6.2 | 0.864 | 5.3 | 4.94 [20] 5.4 [19] |
| | $7p^4+$ | 14.960 | | | | |

lanthanide serie (Nb–Ta, Mo–W, Ru–Os, Rh–Ir, – giving only one point for extrapolation).

For the correlation ratios of $d$ elements we suppose therefore that these can be obtained from correlation ratios of elements between Hf and Hg, by re-calculating, according to Fig. 2. In this figure, the change of correlation ratios, $\Delta_{CR}$, between Hf and 104, Re and 107 and Hg and 112, obtained from direct extrapolation as shown in Fig. 1, is plotted. One can see in Fig. 2, that the

change $\Delta_{CR}$ is approximately in linear dependence to $Z$ between elements $104-112$. Then for 105, 106, 108 and 109 elements we took the correlation ratio values for Ta, W, Os and Ir from Table 5 and corrected them by the corresponding $\Delta_{CR}$ from Fig. 2. Such correlation ratios are also plotted in Fig. 1 (as isolated points). Data for 110 and 111 elements were then obtained as linear interpolation between 109 and 112 elements in Fig. 1.

The described extrapolation yields the "extrapolated correlation ratios" for the $104-120$ element region, as shown in column 5 of Table 6. In this table DHF calculated ionization potentials (eigenvalues) from [3] are also presented for the last two subshells. For 116 element the mean value of both possible extrapolations is used (marked by two points in Fig. 1).

In column 4 of Table 6, the "expected I.P.", i.e. the expected experimental first ionization potential of each element, is presented, calculated using the extrapolated correlation ratio (or mean value of its two possible values) and DHF calculated I.P. as basic data. For comparison, in column 6, the expected I.P. from DFS calculations [1] are presented. In the last column some data [19] and [20] are presented, which were obtained by extrapolation from the trends in the periodic system (without DHF or DFS calculations).

## 5. Discussion

The comparison of our values sometimes shows substantial differences from DFS data [1] and even greater differences from simply extrapolated data [19, 20]. The differences between ours values and data in [1] and [2] are caused by different approximations, used in solution of the Dirac equation. The eigenvalues and total energies in [1] and [2] are apparently obtained by the noncorrected DFS method. The theoretical descriptions of formulae in [1] do not present the corrections $\delta\varepsilon_i$, as shown in Eqs. $(4-6)$ – which could correct the DFS eigenvalues and DFS total energies to more exact values of the MDFS or DHF method. When we compare eigenvalues of valence electrons, published in [1] and [2] with ours, we find them very low because of this noncorrected DFS approximation.

Also the total energies of [1] are similarly noncorrected by formula (6) (as is apparent e.g. for the total energy of $Au^{79}$ in [1] when compared with noncorrected DFS and corrected MDFS values for $Au^{79}$ presented in [4], including the differences for point nucleus in [1] and finite nucleus in [4]). It is natural that the calculated ionization potentials of [1], obtained by "method B" from DFS noncorrected total energies of atom and $1^+$ ion, generally will differ from MDFS or our DHF eigenvalues or ionization potentials (as shown in Table 5 and 6).

For correcting calculated ionization potentials to expected values, only a very briefly tested relation was used in [1]: DFS calculations of ionization potentials for Pt, Au and Hg were correlated to experimental values and gave very optimistic correlation values (found a difference 0.2 eV corresponding to our correlation ratio 0.98). On this basis, to calculate DFS ionization potentials in [1] and [2] $+0.2$ eV was added in the $d$ electron region and $+0.8$ eV (estimated

similarly in the Pb region in [1]) in the p electron region, to correct the calculated ionization potentials to expected experimental values.

Our extrapolation in Figs. 1 and 2 shows, however, that a more complex correction procedure should be applied. In some cases this caused strong differences between our values and the values of ionization potentials calculated in [1]. If we compare the non-corrected ionization potentials as calculated in [1] (i.e. values from [1] after deduction of 0.2 eV or 0.8 eV correction respectively), we see relatively good agreement with our DHF eigenvalues in 115—120 element region. In the region 104—114 the DFS calculated ionization potentials (non-corrected) are systematically lower by $\sim 1$ eV than our calculated DHF values. We believe that our values are more correct than in [1] and [2], and that they are, probably, generally accurate within $\pm 5\%$ when correlation ratios can be extrapolated by the singly way. When two possible extrapolations are used, the accuracy is defined by both correlation ratios as limit values (probably within $\pm 10\%$, see element 116). Elements 104 and 105 are presented in two possible energetically close configurations, each of them using the same correlation ratios.

Generally from the data in Table 6, it is not possible to make a valuable prediction of the chemical behavior of unknown elements. However our results are valuable for mass spectroscopic behavior and some preliminary prediction could be done.

In mass spectrometrical separation of an ore in the search of a superheavy element in the 110—112 element region, one can see from Table 6 that a very strong (electron bombardment) ionization is necessary. The ionization potential of these elements is so high that they could easily be lost (nonionized) during mass separation, when similar Pt, At and Hg are well ionized in the $1^+$ state and collected with good yield. The first ionization potential of 112 element is close to the ionization potential of Kr. From this fact, it is possible that element 112 and perhaps 111 would not follow well the chemistry of Au and Hg, but perhaps would behave mostly as noble metal. A more conclusive basis for prediction may only be given by complete DHF calculations of their different ions and based on the use of Born-Haber cycles.

On the other hand, the mass spectroscopic determination of 104 element should be much easier than for Hf, perhaps as in the cases of $Ca^+$ and $Li^+$. The mass spectroscopic determination of 118 element should be as easy as determination of $Te^+$ or $Po^+$.

The mass spectroscopic ionization and separation of element 119 and 120 should be much less easy than for Cs and Ba, probably similar to Na and Sr. Chemically, the 119 and 120 elements in solution could be probably much less basic than Cs and Ba, perhaps giving $(120)\,SO_4$ soluble as $SrSO_4$.

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