

ATOMIC SPECTROSCOPY

The Energy of Electron Affinity to a Zirconium Atom

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Abstract—Energies and g -factors of the ground states of a zirconium atom and its negative ion and energy of electron affinity to a neutral atom are calculated. The method used represents a combination of the superposition of configurations and the determinant perturbation theory. A satisfactory agreement is obtained between the calculated energy of electron affinity and the experimental value. This shows that the theory can provide an adequate description of complicated multielectron systems. © 2001 MAIK “Nauka/Interperiodica”.

INTRODUCTION

Atoms and ions with several valence electrons and an unfilled d shell are of great interest for atomic physics as well as other fields of physics (astrophysics and reactor physics) [1–3].

In this paper, the energy of electron affinity is calculated for a zirconium atom. To do this, energies of the ground states of a neutral atom and its negative ion should be calculated. The ground configuration of Zr and Zr^- are $1s^2\dots 4p^6 4d^2 5s^2$ and $1s^2\dots 4p^6 4d^3 5s^2$, respectively [2].

The method of superposition of configurations (SC) is one of the most popular methods for calculating complicated polyvalent atoms. This method, which was repeatedly used by our group for the calculation of energy levels and various observables in heavy atoms [4–6], is applicable to Zr atoms as well. All electrons are separated into two parts. $[1s^2\dots 4p^6]$ electrons are related to the core, and $4d$ and $5s$ electrons are left in the valence domain. Because the number of valence electrons is large (four for a neutral atom and five for a negative ion), the dimensions of the configuration space turn out to be so great that diagonalization of the Hamilton matrix becomes impossible. For this reason, Schrödinger’s matrix equation is solved in a certain subspace with the calculation of the second-order correction by the method of the determinant perturbation theory (PT).

The first part of this paper is devoted to the general formalism of the method proposed (the SC method in combination with the determinant PT). In the second part of the work, results of the calculation of ground state energies for Zr and Zr^- are discussed and g -factors are calculated for these states.

GENERAL FORMALISM

As mentioned above, the calculation of the energy of electron affinity for a Zr atom by the SC method

requires the knowledge of the ground state energies of a neutral atom and its negative ion. As usual, this requires the solution of a many-particle Schrödinger’s equation

$$\hat{H}\Psi_n = E_n\Psi_n, \quad (1)$$

where E_n is the energy of the n th level and Ψ_n is the corresponding wave function, which is sought in the form of a linear combination of Slater determinants

$$\Psi_n = \sum_{i=1}^N C_i^{(n)} \det_i. \quad (2)$$

Here, N is the dimensionality of the configuration space and \det_i are determinants constructed from basis orbitals. The latter were found in the following way. Hartree–Fock–Dirac (HFD) equations were solved for the $[1s^2\dots 4p^6]4d^2 5s^2$ configuration of neutral zirconium and for the $[1s^2\dots 4p^6]4d^3 5s^2$ configuration of a negative zirconium ion. Further, in the calculation of Zr, the $[1s^2\dots 4p^6]$ orbitals were frozen and the orbital $5p$ was obtained from the solution of the HFD equation for the $5s^2 5p^2$ configuration.

The remaining orbitals were constructed virtually. The method for constructing virtual orbitals is described in detail in [5]. As a result, the complete basis set includes the orbitals 1–15s, 2–15p, 3–15d, 4–15f, 5–15g, where the numbers indicate the principal quantum numbers.

For Zr^- , we have the following Hartree–Fock orbitals: $4d$ and $5s$ for the $4d^3 5s^2$ configuration and $5p$ for the $4d 5s^2 5p$ configuration. The remaining orbitals are virtual. The complete basis set includes the orbitals 1–15s, 2–15p, 3–15d, 4–16f, and 5–16g. Now substituting (2) into (1) and varying over the coefficients $C_i^{(n)}$, we obtain

$$\sum_k H_{ik} C_k^{(n)} = E_n C_i^{(n)}$$

or in the matrix form

$$H\Phi_n = E_n\Phi_n, \quad (3)$$

where H is the energy matrix and $\Phi_n = (C_1^{(n)}, C_2^{(n)}, \dots, C_N^{(n)})$ is the desired wave function written in the basis of determinants.

If a complete superposition of configurations is carried out by using all the basis functions, the dimensionality of the configuration space will be $\sim 4 \times 10^9$ for Zr and $\sim 5 \times 10^{11}$ for Zr⁻. The solution of matrix equation (3) of this dimensionality considerably exceeds modern computational resources. In this connection, the most important configurations should be selected. The number of determinants taken into account in these configurations is $\sim 4 \times 10^6$. Because it is rather difficult to solve equation (3) of even this dimensionality, the configuration space of N determinants was divided in two parts: $N = N_0 + N_1$. For the first part of the configuration space of dimensionality ($N_0 \times N_0$), the problem was solved by the SC method and the second part was taken into account within the framework of the determinant PT. Note that the choice of N_0 is arbitrary to a certain extent and is determined so that, first, the possibility of using the SC method to find first solutions of Schrödinger's equation for this part of the configuration space is retained and, second, the correction of the determinant PT is as small as possible.

Within the framework of this approach, we represent the matrix H in the form

$$H = H_0 + H_1,$$

where the matrix H_0 in turn is conveniently represented as

$$H_0 = H'_0 + D. \quad (4)$$

Here, H'_0 is the left upper block of the matrix H of dimensionality $N_0 \times N_0$ and D is the diagonal of the block of dimensionality $N_1 \times N_1$ of the matrix H with elements ($H_{N_0+1N_0+1}, \dots, H_{NN}$).

It is clear that, if N_0 is taken large enough and the configurations in (2) are ordered so that those producing the greatest contribution fall within H'_0 , then H'_0 prevails over H_1 . This allows H_1 to be taken into account within the framework of the perturbation theory. The matrix H'_0 will be called the initial approximation for the determinant PT.

At the first stage, we solve the matrix equation

$$H_0\Phi_n^0 = E_n^0\Phi_n^0. \quad (5)$$

Here, $\Phi_n^0 = (C_1^{(n)}, C_2^{(n)}, \dots, C_{N_0}^{(n)}, 0, \dots, 0)$ for $n \leq N_0$ and $\Phi_n^0 = (0, \dots, 0, 1, 0, \dots, 0)$ for $n > N_0$. The unit occupies the n th position. The choice of configurations for the initial approximation is discussed in detail in the next

section. Solving Eq. (5), we find the energies and the wave functions. All configurations are rearranged in accordance with their weight contribution to the wave functions in decreasing order. The weight of configurations is determined by the expression

$$W_k = \sum_{i=1}^{N_k} |C_i^{(k)}|^2.$$

Here, N_k is the number of determinants in the k th configuration and $C_i^{(k)}$ are the corresponding coefficients. Configurations with weights lower than a certain threshold value ($\sim 10^{-5}$ – 10^{-6}) are rejected. Instead of rejected configurations, other ones are added and Eq. (5) is solved, again producing new eigenvectors and energy eigenvalues. Repeating this procedure several times, we finally obtain the matrix of the initial approximation H'_0 and the corresponding wave functions Φ_n^0 , which take into account configurations producing the greatest contribution. All the rejected configurations are then taken into account by using the determinant PT.

As we are interested only in the energy of the ground state (i.e., the first eigenvalue of the equation), there is no need to using the direct diagonalization method. To find a few first eigenvalues and eigenvectors, we use the Davidson method (see, for example, [7]). Eigenvalues of a matrix of a dimensionality of $\sim 2 \times 10^5$ are found within the framework of this method.

At the second stage, the contribution of H_1 is taken into account. It is easy to see that the first-order correction to the unperturbed energy E^0 is

$$\delta_i^{(1)} = \langle \Phi_i^0 | H_1 | \Phi_i^0 \rangle = 0,$$

and the second-order correction can be calculated from the formula

$$\delta_i^{(2)} = \sum_{k=N_0+1}^N \frac{\langle \Phi_i^0 | H_1 | \Phi_k^0 \rangle \langle \Phi_k^0 | H_1 | \Phi_i^0 \rangle}{E_i^0 - E_k^0}, \quad (6)$$

where E_k^0 is the k th element of the diagonal D [see formula (4)]. It is seen from (6) that there is no need to construct a complete matrix H of dimensionality N . It will suffice to construct the initial approximation matrix H'_0 of dimensionality N_0 , diagonal elements of the block of dimensionality N_1 , and two symmetric rectangular blocks of dimensionality $N_1 \times N_0$ of the matrix H .

This method has the following advantages. First, if $N \gg N_0$, the block of dimensionality $N_1 \times N_0$ to be constructed will be much smaller than the block of dimensionality $N_1 \times N_1$. Second, by virtue of additivity, the sum in (6) can be divided into a series of subsums; i.e., with knowledge of the initial approximation (the unper-

Table 1. Valence energy of the ground state ${}^3F_2(4d^25s^2)$ for Zr

Method	N_c	N_0	E_v , au	δ , au
SC(S_1)	2646	92207	2.808875	
SC(S_2)	3903	135652	2.809172	0.000297
SC(S_1) + PT($S_2 - S_1$)	3903	135652	2.809216	0.000341

Note to Tables 1 and 2: N_c and N_0 are the numbers of configurations and determinants, respectively, taken into account; E_v is the valence energy of the ground state; and δ is the correction to $E_v(S_1)$.

Table 2. Valence energy of the ground state ${}^4F_{3/2}(4d^35s^2)$ for Zr^-

Method	N_c	N_0	E_v , au	δ , au
SC(S_1)	2227	162447	2.835419	
SC(S_2)	2810	209396	2.837245	0.001826
SC(S_1) + PT($S_2 - S_1$)	2810	209396	2.837552	0.002133

turbed energy E_i^0), all second-order corrections can be taken into account in parts.

RESULTS AND DISCUSSION

The energy of electron affinity E_A to a zirconium atom can be defined as

$$E_A = \Delta E_{\text{core}} + \Delta E_{\text{val}},$$

where ΔE_{core} and ΔE_{val} are the differences between the corresponding core and total valence energies of the ground states of Zr^- and Zr. By virtue of the fact that the bases for a neutral atom and its negative ion were constructed in different ways, the absolute values of core energies for them are different:

$$E_{\text{core}}(\text{Zr}) = 3594.3696 \text{ au},$$

$$E_{\text{core}}(\text{Zr}^-) = 3594.3488 \text{ au},$$

$$\Delta E_{\text{core}} = -0.0208 \text{ au}. \quad (7)$$

Note that the core–valence correlations are not taken into account here. At present, methods for accurate calculation of correlations of this type in atoms with 4–5 valence electrons are unavailable. Therefore, we could only estimate the corresponding contribution to the affinity energy, which is ~ 0.005 au. Thus, the problem is to take into account most completely the interaction of valence electrons and to calculate ΔE_{val} .

Once the matrix H_0' is constructed and the wave function Φ^0 is found, formula (6) of the determinant PT is used in further calculations. In this connection, its accuracy should be estimated. This is carried out as follows.

Two calculations of valence energies of the ground states E_v were made for both Zr and Zr^- by the SC method on sets of configurations S_1 and S_2 , where $S_1 \subset$

S_2 . Then for the second set we carried out a calculation by the determinant PT method with the initial approximation corresponding to the set S_1 . This allowed us to determine the error of the PT for the set S_2 (see Tables 1 and 2).

The first basis set S_1 for Zr included one-, two-, and three-particle excitations from the ground state $Zr(4d^25s^2)$ to the shells 5–8s, 5–7p, 4–7d, 4–7f, and 5–7g and one- and two-particle excitations to the shells 5–9s, 5–9p, 4–9d, 4–9f, and 5–9g. Configurations with weights lower than 10^{-5} were rejected. In the construction of S_2 , it is very important that configurations from the first set S_1 be completely entered into S_2 . Therefore, the second set S_2 was constructed merely of S_1 by one-particle excitations to the shells 5–9s, 5–9p, 4–9d, 4–9f, and 5–9g. Then configurations with weights lower than 10^{-6} were rejected. It is seen from Table 1 that the error of the PT method is about 15%.

The first set S_1 for Zr^- included one-, two-, and three-particle excitations from the ground state to the shells 5–8s, 5–6p, 4–6d, 4–5f, and 5g and one- and two-particle excitations to the shells 5–10s, 5–10p, 4–10d, 4–10f, and 5–7g. The second set S_2 was constructed of S_1 by one-particle excitations to the shells 5–12s, 5–12p, 4–12d, 4–14f, and 5–8g. Configurations with weights lower than 10^{-5} were rejected in both sets. It is seen from Table 2 that the error of the PT method is about 17%.

One can see that the accuracy of the PT is somewhat worse in the case of an ion, which corresponds to a greater absolute value of the correction. In the final calculation presented below, PT corrections are still greater. Therefore, we estimate the accuracy of the PT as 40%.

The valence energy of the first set S_1 , i.e., $E_v^0 = E_v(S_1)$, was taken as the initial approximation for the

Table 3. PT corrections for various configuration sets for Zr (3F_2 level) ($N_c = N_c^0 + N_c^1$, where $N_c^0 = 2646$)

Shells	m	N_c^1	δ_{pt} , au
9spdfg	1–4	29827	0.000743
10spdfg	1, 2	1443	0.000183
11spdfg	1, 2	1689	0.000195
12spdfg	1, 2	1935	0.000179
13spdfg	1, 2	2181	0.000150
14spdfg	1, 2	2427	0.000109
15spdfg	1, 2	2673	0.000071
Total	1–4	42175	0.001630

Note to Tables 3 and 4: N_c is the total number of configurations, δ_{pt} is the PT correction, and m is the multiplicity of excitations from the ground state to the shells.

Table 4. PT corrections for various configuration sets for Zr^- (${}^4F_{3/2}$ level) ($N_c = N_c^0 + N_c^1$, where $N_c^0 = 2227$)

Shells	m	N_c^1	δ_{pt} , au
12spd, 14f, 8g	1–4	61435	0.006284
13spd, 9, 10g	1, 2	3000	0.000642
11, 12g	1, 2	1506	0.000455
13, 14g	1, 2	1650	0.000246
15, 16g	1, 2	2010	0.000111
14spd, 15f	1, 2	2754	0.000135
15spd, 16f	1, 2	3195	0.000088
8sp, 7df, 8g	5	1405	0.000075
Total	1–5	79955	0.008678

final calculation for both Zr and Zr^- . As noted above, by using the additivity property, we divide the total set of configurations in a series of subsets, where the latter are added each time to the initial approximation selected. Each next subset of configurations corresponds to excitations to higher shells and does not include the preceding ones.

Contributions of subsets to PT corrections to energies for Zr and Zr^- are presented in Tables 3 and 4, respectively.

Thus, a total of 42175 configurations (see Table 3) obtained by exciting electrons from the ground state to shells up to 15spdfg was taken into account for Zr. All one- and two-particle excitations were taken into

account as were the most important three- and four-particle excitations. The total PT correction to the valence energy of the ground state $E_v(\text{Zr})$ is 0.00163 au.

A total of 79955 configurations and excitations to the shells up to 15spd, 16fg were taken into account in the framework of PT for Zr^- (Table 4). Complete allowance was made for single and double excitations from the ground state to these shells and partial allowance was made for triple, fourfold, and fivefold excitations. The total PT correction to the valence energy $E_v(\text{Zr}^-)$ is 0.00868 au.

PT correction relative to the initial approximation $E_v(S_1)$ can be refined somewhat for Zr and Zr^- by including results from Tables 1 and 2. The total PT correction can be decreased by the difference $\delta(\text{SC}(S_1) + \text{PT}(S_2 - S_1)) - \delta(\text{SC}(S_2))$ (see Tables 1 and 2). Thus, we have

$$\delta_{\text{pt}}(\text{Zr}) = 0.00159,$$

$$\delta_{\text{pt}}(\text{Zr}^-) = 0.00837.$$

The total valence energy consists of the sum of the valence energy of the initial approximation and the total PT correction

$$E_{\text{val}} = E_v(S_1) + \delta_{\text{pt}}. \quad (8)$$

Let us add and subtract $E_v(S_2)$. Then formula (8) can be written in the form

$$E_{\text{val}} = E_v(S_2) + (\delta_{\text{pt}} - E_v(S_2) + E_v(S_1)). \quad (9)$$

We denote the second term in (9) as $\widetilde{\delta}_{\text{pt}}$

$$\widetilde{\delta}_{\text{pt}} = \delta_{\text{pt}} - E_v(S_2) + E_v(S_1). \quad (10)$$

Then ΔE_{val} can be represented as

$$\Delta E_{\text{val}} = \Delta E_v(S_2) + \Delta \widetilde{\delta}_{\text{pt}}. \quad (11)$$

Taking into account the variation of the core energy (7), formulas (9)–(11), and data from Tables 1 and 2, we finally find for the affinity energy E_A

$$E_A = \Delta E_{\text{core}} + \Delta E_v(S_2) + \Delta \widetilde{\delta}_{\text{pt}} \quad (12)$$

$$= -0.0208 + 0.0281 + 0.0053 = 0.0126 \text{ au.}$$

As seen from (12), all the three terms are very important and none of them can be neglected. We estimate the error in our calculation of the valence energy at a level of 0.002 au and assign it to incompleteness of the configuration space and inaccuracy of the second-order correction taken into account within the framework of the PT. Another theoretical uncertainty noted above is associated with core–valence correlations. Within the limits of this uncertainty, our result agrees with an experimental value of $0.0157 \pm 0.0005 \text{ au} = 0.427 \pm 0.014 \text{ eV}$ [2].

We also calculated g -factors of the ground states of Zr and Zr⁻:

$$g(\text{Zr}) = 0.670,$$

$$g(\text{Zr}^-) = 0.402.$$

Knowing that the ground states of Zr and Zr⁻ are determined by the terms 3F_2 and $^4F_{3/2}$, respectively, their g -factors can be calculated by using general rules of LS -coupling. These values turn out to be in very good agreement with the numerical calculation and with the experimental value for zirconium $g(\text{Zr}) = 0.66$ [8].

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