

## ASYMPTOTIC ELECTRON WAVEFUNCTIONS OF EXCITED ATOMS

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**Abstract.** The method developed earlier by N. Vitanov and G. Panev [2] for determination of the constant  $A$ , involved in the asymptotic electron wavefunction in the atom at large distances from the nucleus, is applied for the lowest excited states of a number of neutral atoms.

**Резюме.** Предложенный раньше метод (Н. Витанов и Г. Панев [2]) для определения константы  $A$  входящей в асимптотическую волновую функцию внешнего электрона в атоме на больших расстояниях от ядра, применен для низких возбужденных состояниях некоторых атомов.

### 1. Introduction

In many elementary processes in the atomic-particle collisions, such as charge-transfer, ionization, excitation etc., the electron transitions occur at large distances between the particles compared to their sizes. The cross-sections of these processes depend on the asymptotic behaviour at large distances of electron wavefunctions in both atomic particles.

The exact asymptotic wavefunction  $\psi(r)$  of an outer electron in the atom at large distances between the electron and the nucleus compared to the core size is the solution of the Schrödinger equation (the atomic units are used everywhere)

$$-\frac{1}{2}\nabla^2\psi - \frac{1}{r}\psi = -\frac{1}{2}\gamma^2\psi, \quad r \rightarrow \infty,$$

and has the form:

$$\psi(r) = R^\infty(r)Y_{im}(\theta, \varphi)$$

where  $Y_{im}(\theta, \varphi)$  is the normalized spherical function,  $i$  and  $m$  are the electron orbital momentum and its projection respectively, and  $-\gamma^2/2$  is the electron binding energy, i.e. the ionization potential of the atom.

The exact asymptotic radial wavefunction  $R^\infty(r)$  is expressed by the Whittaker function  $W_{1/\gamma, i+1/2}(2\sigma r)$  and at large distances it is given by the asymptotic power series:

$$R^\infty(r) = Ar^{1/\gamma-1}e^{-\gamma r} = \sum_{n=0}^{\infty} \frac{1}{(2\gamma r)^n n!} \prod_{k=1}^n (i-1/\gamma+k)(i+1/\gamma+1-k). \quad (1)$$

All parameters of the asymptotic radial wavefunction  $R^\infty(r)$  are well known ( $i$  exactly,  $\gamma$  with great accuracy) except for the asymptotic constant  $A$ .

The constant  $A$  can be determined by the quantum defect theory of Seaton [1]. The theory gives an expression for  $A$  which involves the derivative  $d\mu/d\nu$  of the quantum defect  $\mu$  with respect to the effective quantum number  $\nu = 1/\gamma$ . This derivative is determined empirically, which requires a thorough knowledge of the energy levels of the atomic particle. Hence, this method fails when the distance between the neighbouring levels is large and therefore the derivative  $d\mu/d\nu$  cannot be obtained, i.e. the quantum defect method fails for the ground state and for the lowest excited states.

In our previous work [2] we have developed a new method for determination of the asymptotic constant  $A$  and we have presented the calculated values of this constant for the *ground-state* wavefunctions of the neutral atoms, positive ions and negative ions with atomic numbers  $2 \leq Z \leq 54$ . Until now, no data are available in the literature for the constant  $A$  for the lowest excited states of the neutral atoms (except for the work of Matic et al. [3]). In section 2 we briefly review the method developed in [2] and in section 3 we present the values of  $A$  calculated by this method for the lowest excited states of a number of neutral atoms.

## 2. Review of the Method

The method developed in [2] is based on matching the asymptotic wavefunction  $R^\infty(r)$  to the wavefunction  $R_{\text{HF}}(r)$  obtained by the self-consistent Hartree-Fock method [4], in the region where both wavefunctions are valid. In view of the difference between the exact (spectroscopic) value  $-\gamma^2/2$  of the electron energy and the "self-consistent" value  $-\gamma_{\text{HF}}^2/2$  obtained by the Hartree-Fock procedure, the constant  $A$  is obtained in two steps. In the first step we calculate the Hartree-Fock's asymptotic constant  $A_{\text{HF}}$  related to the asymptotic wavefunction with the Hartree-Fock's energy  $-\gamma_{\text{HF}}^2/2$ , and in the second step we determine  $A$  through a relationship between  $A$  and  $A_{\text{HF}}$  (Eq. (5)).

(i) In the matching region the Hartree-Fock wavefunction  $R_{\text{HF}}(r)$  is not fitted to the exact asymptotic wavefunction  $R^\infty(r)$  describing the behaviour of an electron of energy  $-\gamma^2/2$ , but to the asymptotic wavefunction  $R_{\text{HF}}^\infty(r)$  which describes the behaviour of an electron of Hartree-Fock's energy  $-\gamma_{\text{HF}}^2/2$  at large distances from the nucleus.  $R_{\text{HF}}^\infty(r)$  is a solution of an equation like  $R^\infty(r)$  and has the same form,

but with  $A_{\text{HF}}$  and  $\gamma_{\text{HF}}$  instead of  $A$  and  $\gamma$ :

$$R_{\text{HF}}^{\infty}(r) = A_{\text{HF}} r^{1/\gamma_{\text{HF}}-1} e^{-\gamma_{\text{HF}} r} \sum_{n=0}^{\infty} \frac{1}{(2\gamma_{\text{HF}} r)^n n!} \times \prod_{k=1}^n (i - 1/\gamma_{\text{HF}} + k)(i + 1/\gamma_{\text{HF}} + 1 - k). \quad (2)$$

Assuming that the radial wavefunction  $\mathfrak{R}(r)$  of an electron of energy  $-\gamma_{\text{HF}}^2/2$  is given by the representation:

$$\mathfrak{R}(r) = \begin{cases} R_{\text{HF}}(r), & r \leq r_m \\ R_{\text{HF}}^{\infty}(r), & r > r_m \end{cases}$$

where  $r_m$  is the matching point, we require, on one hand, the continuity condition

$$R_{\text{HF}}(r_m) = R_{\text{HF}}^{\infty}(r_m) \quad (3)$$

for  $\mathfrak{R}(r)$  to be performed, from which we obtain the "continuity" constant  $A_{\text{HF}}^c$ , which is obviously a function of  $r_m$ , i.e.

$$A_{\text{HF}}^c = A_{\text{HF}}^c(r_m).$$

On the other hand, we require the normalization condition

$$1 = \int_0^{\infty} |\mathfrak{R}(r)|^2 r^2 dr = \int_0^{r_m} |R_{\text{HF}}(r)|^2 r^2 dr + \int_{r_m}^{\infty} |R_{\text{HF}}^{\infty}(r)|^2 r^2 dr \quad (4)$$

to be performed. Then by a numerical integration we gain the "normalization" constant  $A_{\text{HF}}^n$ , which is also a function of  $r_m$ , i.e.  $A_{\text{HF}}^n = A_{\text{HF}}^n(r_m)$ .

The constant  $A_{\text{HF}}$  is obtained in the point  $r_m = r_0$  where

$$A_{\text{HF}}^c(r_0) = A_{\text{HF}}^n(r_0)$$

which ensures both the continuity condition (3) and the normalization condition (4) for  $\mathfrak{R}(r)$  to be performed. If such a point does not exist, the constant  $A_{\text{HF}}$  is calculated where the curves  $A_{\text{HF}}^c(r_m)$  and  $A_{\text{HF}}^n(r_m)$  are most close to one another.

(ii) The relationship between  $A_{\text{HF}}$  and  $A$  can be found analysing the above equations, where  $R^{\infty}(r)$  and  $R_{\text{HF}}^{\infty}(r)$  are their solutions [5]:

$$A = A_{\text{HF}}(\gamma/\gamma_{\text{HF}})^{1/2+1/\gamma_{\text{HF}}}.$$

### 3. Results

Using this method, we have calculated the values of  $A$  for the lowest excited states of a number of neutral atoms for which the Hartree-Fock wavefunctions are available. The values of  $A$  are presented in Table 1. They are calculated by taking into account the first two terms of the asymptotic expansions (1) and (2). As the analysis shows,

**Table 1.** Values of the constant  $A$  for some excited atoms. The value of  $A$  for the lowest level of a given multiplet is presented. The values for the other levels of the multiplet can be determined from the presented ones by using Eq. (5). In most cases the differences are very small.

Atom	Valence electron configuration and excited-state term	Electron state	$A$
C	$2p^2 \quad -^1D_2$	2p	1.02
C	$2p^2 \quad -^1S_0$	2p	0.70
N	$2p^3 \quad -^2D_{5/2}$	2p	1.27
N	$2p^3 \quad -^2P_{1/2}$	2p	1.09
O	$2p^4 \quad -^1D_2$	2p	1.20
O	$2p^4 \quad -^1S_0$	2p	0.96
Si	$3p^2 \quad -^1D_2$	3p	0.83
Si	$3p^2 \quad -^1S_0$	3p	0.55
P	$3p^3 \quad -^2D_{3/2}$	3p	1.24
P	$3p^3 \quad -^2P_{1/2}$	3p	1.02
S	$3p^4 \quad -^1D_2$	3p	1.31
S	$3p^4 \quad -^1S_0$	3p	1.00
Sc	$3d^2 4s^1 \quad -^4F_{3/2}$	4s	0.86
Ti	$3d^3 4s^1 \quad -^5F_1$	4s	1.02
Ti	$3d^2 4s^2 \quad -^1G_4$	4s	0.95
Ti	$3d^2 4s^2 \quad -^1D_2$	4s	1.05
Ti	$3d^2 4s^2 \quad -^3P_0$	4s	1.03
V	$3d^4 4s^1 \quad -^6D_{1/2}$	4s	1.11
V	$3d^3 4s^2 \quad -^2G_{7/2}$	4s	0.97
V	$3d^3 4s^2 \quad -^4P_{1/2}$	4s	1.00
Cr	$3d^4 4s^2 \quad -^5D_0$	4s	1.05
Mn	$3d^6 4s^1 \quad -^6D_{9/2}$	4s	0.91
Fe	$3d^7 4s^1 \quad -^5F_5$	4s	1.19
Co	$3d^8 4s^1 \quad -^4F_{9/2}$	4s	1.25
Co	$3d^7 4s^2 \quad -^4P_{5/2}$	4s	1.15
Ni	$3d^9 4s^1 \quad -^3D_3$	4s	1.26
Ni	$3d^8 4s^2 \quad -^1G_4$	4s	0.94
Ni	$3d^8 4s^2 \quad -^1D_2$	4s	1.13
Ni	$3d^8 4s^2 \quad -^3P_2$	4s	1.08
Cu	$3d^9 4s^2 \quad -^2D_{5/2}$	4s	1.20
Ge	$4p^2 \quad -^1D_2$	4p	0.80
As	$4p^3 \quad -^2D_{3/2}$	4p	1.21
As	$4p^3 \quad -^2P_{1/2}$	4p	0.96
Se	$4p^4 \quad -^4D_2$	4p	1.29
Se	$4p^4 \quad -^1S_0$	4p	0.96
Y	$4d^2 5s^1 \quad -^4F_{3/2}$	5s	0.84
Zr	$4d^3 5s^1 \quad -^5F_1$	5s	1.12
Nb	$4d^3 5s^2 \quad -^4F_{3/2}$	5s	1.22
Mo	$4d^4 5s^2 \quad -^5D_0$	5s	1.05
Tc	$4d^6 5s^1 \quad -^6D_{9/2}$	5s	1.24
Rh	$4d^9 \quad -^2D_{5/2}$	4d	0.30
Pd	$4d^9 5s^1 \quad -^3D_3$	5s	1.26
Ag	$4d^9 5s^2 \quad -^2D_{5/2}$	5s	0.74

the next terms can be neglected. The Hartree-Fock wavefunctions and energies are taken from [4] and the exact (spectroscopic) electron energies  $-\gamma^2/2$  are taken from [6].

In addition, we have to note that there are no restrictions to apply this method to any excited state if the corresponding Hartree-Fock wavefunction is available, but the inaccuracy of the Hartree-Fock wavefunctions for the higher excited states makes it inappropriate in these cases; then the quantum defect theory of Seaton is preferable.

The results obtained in this work can be of real importance in any case when the asymptotic electron wavefunction is needed for the description of a given process. Such a case is, for example, the multi-state charge-transfer theory used for the description of the charge-transfer processes in which the channels with the lowest excited states of the involved atoms and ions cannot be neglected. The matrix elements needed in this approach involve the electron wavefunctions of the initial and the final states of the system of the two atomic particles, which in the diabatic representation can be expressed by the asymptotic electron wavefunctions of two atomic particles. The same situation arises in the theory of other processes between atomic particles, such as ionization, excitation, etc.

## References

- 1 M. J. Seaton. *Mon. Not. R. Astron. Soc.* **118** (1958) 504.
- 2 N. Vitanov, G. Panev. *Europhys. Lett.* **16** (1991) 159.
- 3 M. Matic, V. Sidis, M. Vujovic, B. Cobic. *Bulg. J. Phys.* **13** (1980) 3665.
- 4 E. Clementi, C. Roetti. *At. Data Nucl. Data Tables* **14** (1974) 177.
- 5 A. V. Evseev, A. A. Radzig, B. M. Smirnov. *Opt. Spectrosc.* **44** (1978) 833.
- 6 A. A. Radzig, B. M. Smirnov. *Reference Data of Atoms, Molecules and Ions* (Springer-Verlag, Berlin 1985).