The submitted manuscript has been accepted by a contractor of the U. S. Government under contract No. W-31-109-Eng-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

A SIMPLE FORMULA FOR THE ENERGIES OF DOUBLY EXCITED STATES*

Chii-Dong LIN**

Argonne National Laboratory, Argonne, IL 60439 USA

CONF-861114--52

DE87 004742

and

S. WATANABE

Observatoire de Paris-Meudon, 92190 Meudon, France

ABSTRACT

A simple formula for the energy levels of doubly excited states of atoms and multiply charged ions is derived and expressed in terms of a set of new correlation quantum numbers. The accuracy of the formula is checked by comparing with the results from other elaborate calculations. Modification of the formula for doubly excited states of multielectron atoms are also presented.

*Work is supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract W-31-109-Eng-38.

**Permanent Address: Department of Physics, Kansas State University, Manhattan, Kansas 66506 USA.

MASTER

INTRODUCTION

In recent years doubly excited states of atoms and ions have been observed in photon-, electron- and ion-impact collisions with atoms. In particular, for collisions between multiply charged ions with multielectron atoms, doubly excited states are produced in abundance via double electron capture, or via simultaneous excitation and charge transfer processes. Despite the intensive studies in the past, [1] our understanding of doubly excited states is still quite limited. Today, the energy levels of most doubly excited states of atoms and ions of two-electron systems are still unknown. Extensive calculations have been completed only for some low-lying doubly excited states of helium and several low-Z ions. Lack of the knowledge of the energy levels of doubly excited states makes it difficult in the interpretation of collision data such as those obtained in energy-gain spectra [2] or in the zero-degree spectroscopy [3].

In this paper, we derive a simple approximate formula for estimating the energy levels of a certain class of doubly excited states of atoms based on our current understanding of the correlations of doubly excited states [4].

According to the new classification scheme, [4] all doubly excited states of a two-electron atom or ion are designated as ${}_n^{(K,T)}_N^A 2S + 1 L^\pi$, where K, T and A are the correlation quantum numbers, n and N are similar to the principal quantum numbers of the outer and inner electrons, respectively. For intrashell states, $n = N$ and for intershell states we adopt $n > N$. The other L, S and π quantum numbers have their usual meanings. The states designated by this scheme can be grouped into different series. By varying n only and keeping all of the rest of the quantum numbers fixed, we arrive at a usual Rydberg series converging to the N-th hydrogenic limit of the one-electron ion. The energy levels can also be grouped according to the $(K,T)^A$

quantum numbers with fixed n and N . In this case, they form rotor-like supermultiplet structures [4]. One can also find regularity by grouping intrashell states along N for fixed L , S and π . For example, such a series can be formed by the states ${}_N^{(N-1,0)+} 1S^e$. This series is often designated as $Ns^2 1s^e$, even though inappropriate, according to the independent particle picture. This is an example of the 'double Rydberg series' observed in electron-helium collisions [5]. States in this series with large N were attributed to evolve into the Wannier continuum state responsible for the double ionization. Many other series can be similarly formed.

According to the new classification scheme, the K , T and A quantum numbers are assigned according to the rules:[6]

$$T = 0, 1, 2, \dots, \min(L, N-1)$$

$$K = (N-1-T), (N-3-T), \dots, -(N-1-T)$$

(1)

$$\text{and} \quad A = \pi(-1)^{S+T} \quad K > L-N$$

$$= 0 \quad K \leq L-N$$

These rules allow one to enumerate all the K ; T and A quantum numbers for a given L , S , π and N . For the details of the illustration of the correlation patterns implied by these quantum numbers, the readers are referred to the original papers [4]. Roughly speaking, K defines the angular correlation of the two electrons. For a given N , the largest K is $K_{\max} = N - 1$. For states with $K = N - 1$, the two electrons tend to stay on opposite sides of the nucleus and the angle of the two electrons with respect to the nucleus θ_{12}

peaks at 180° . As K decreases, the angle θ_{12} becomes smaller. For $K=0$, θ_{12} is nearly 90° and for negative K the two electrons are on the same side of the nucleus. The quantum number T is the projection of the angular momentum L along the interelectronic axis and A has to do with the joint radial motion of the two electrons. For $A = +1$, the two electrons move toward or away from the nucleus in phase, while for $A = -1$, the radial motion is out of phase such that when one moves in the other moves out and vice versa. For states with $A = 0$, there is no radial correlation between the two electrons. All intrashell states have $A = +1$, while intershell states are distinguished by $A = +1, -1$ and 0 .

DERIVATION of the Formula

We next derive the approximate energy level formula for intrashell states. Starting with the two-electron nonrelativistic Hamiltonian (in atomic units)

$$H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (2)$$

where r_1 and r_2 are the distances of the two electrons from the nucleus and r_{12} is the interelectronic distance and Z is the charge of the nucleus. We can rewrite eq. (2) as

$$H = \left(-\frac{1}{2} \nabla_1^2 - \frac{Z^*}{r_1}\right) + \left(-\frac{1}{2} \nabla_2^2 - \frac{Z^*}{r_2}\right) + (Z^* - Z) \left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \quad (3)$$

where Z^* is an effective charge to be determined variationally. For intrashell states we may take $\langle 1/r_1 \rangle = \langle 1/r_2 \rangle = \langle 1/r \rangle$ and use the one-electron expectation value $\langle 1/r \rangle = Z^*/N^2$. An estimate of $\langle 1/r_{12} \rangle$ stems from an approximation $\langle 1/r_{12} \rangle = \langle 1/r \rangle / (2 - 2\langle \cos\theta_{12} \rangle)^{1/2}$. By taking the expectation value of eq. (3) and minimize the energy with respect to Z^* , we obtain

$$Z^* = Z - \sigma = Z - \frac{1}{2(2 - 2\langle \cos\theta_{12} \rangle)^{1/2}} \quad (4)$$

and the energy is

$$E = - \frac{(Z - \sigma)^2}{N^2} \quad (\text{in a.u.}). \quad (5)$$

This simple eq. (5) gives the energy levels of intrashell states in terms of the average value of $\cos\theta_{12}$ which is characterized by the angular correlation quantum number K and T . In the derivation we have used $\langle 1/r_1 \rangle = \langle 1/r_2 \rangle$ which limits us to apply this formula to intrashell states only. If we were to do a configuration interaction (CI) calculation, this would mean that we include only $NlNl'$ configurations.

Approximate expression for $\langle \cos\theta_{12} \rangle$ has been derived by different authors using the SO_4 group theory. The simplest one gives [7].

$$\sigma = \frac{1}{2(2 + 3K/N)^{1/2}} \quad (6)$$

where the dependence on T is not included. An alternative expression for $\langle \cos\theta_{12} \rangle$ has been given by Herrick et al [8] from which one obtains

$$\sigma = \frac{2}{(24 + \frac{2}{N^2}[7(N+K-1)(N+K+1) + 7T^2 - 6L(L+1) + 12])^{1/2}} \quad (7)$$

A somewhat related expression has also been derived by Crane and Armstrong [9] where they derived an expression for $\langle r_{12}^{-2} \rangle$ from which the expectation value of $1/\langle r_{12} \rangle$ is approximated as $1/\langle r_{12}^{-2} \rangle^{1/2}$. This latter method was used by Crance and Armstrong [9] to compute the energy levels of intrashell states of He and by Rau [10] for H^- .

ENERGIES for Intrashell States

Before we compare the accuracy of eq. (5) using σ given by eq. (6) or eq. (7), we have to discuss its limitations. We note that the equation has been derived for intrashell states only. However, not all $n=N$ states are well described by linear combinations of $NlNl'$ configurations. In fact, for intrashell states where K is negative, previous studies have shown that mixing with intershell states is important. This is not unexpected since for negative K states, the two electrons are on the same side of the nucleus. To reduce the strong electron-electron repulsion, the two electrons have to maintain at $r_1 \neq r_2$, thus requiring intershell states in the CI calculation. Thus we expect that eq. (5) becomes less valid as K becomes smaller. Fortunately, almost all the doubly excited states observed by photon and electron impacts on atoms indicate that only doubly excited states with $A = +1$ and large positive K are produced in the collision. The situation for heavy ion impact is less clear. The energy resolution from the latter measurements so far is incapable of resolving individual doubly states.

In Table I we show the comparison of energy levels calculated using eq. (5) with those obtained from the CI calculations of Bachau [11]. We note that the agreement in all cases is better than one electron volt. This accuracy is adequate for the purpose of identifying doubly excited states

observed in energy-gain spectroscopy. Since the relative energy levels of doubly excited states follows the supermultiplet structure, this also allows us to identify individual states.

ENERGIES for Intershell States

Doubly excited states which have different n but identical N , K , T , A , L , S and π belong to the same channel. For neutral atoms and ions for which $A = +1$, states with n ranging from N to infinite form a Rydberg series. According to the Ritz-Rydberg formula, the energy level for the whole series can be expressed as

$$E(n, N) = E_N - \frac{(Z-1)^2}{2(n-d)^2} \quad (8)$$

where $E_N = -Z^2/2N^2$ is the N -th hydrogenic energy level and d is the quantum defect of the series. By recognizing that the quantum defect for each series is almost constant, we can combine eqs.(5) and (8) to obtain intershell state energies for the $A=+1$ channels. To do this, one calculates the energy of the intrashell state of the series using eq.(5) and fits the result into eq.(8) from which the quantum defect d for the series can be obtained. The energies of all intershell states of the series is then obtained for whatever values of n desired. In Table II we show the comparison of some intershell state energies using this simple method with the calculated results by Lipsky et al [12].

At present, there is no simple method available for estimating the energies of intershell states for which $A = -1$ and $A = 0$.

DOUBLY Excited States of Multi-Electron Atoms

Doubly excited states of multi-electron atoms consist of an electron pair outside a compact open-shell core. The correlated motion of the two outer electrons is similar to the correlation of doubly excited states of two electron atoms. To describe doubly excited states of multielectron atoms, we modify eq.(5) by replacing N by $N^* = N - \mu$. This is equivalent to replacing $\langle 1/r \rangle$ by Z^*/N^{*2} . This leads to the formula

$$E(N, N) = E_{\text{core}} - \frac{(Z - \sigma)^2}{(N - \mu)^2} \text{ (a.u.)}. \quad (9)$$

where E_{core} is the energy of the frozen-core ion. Thus the effect of the penetration of the two outer electrons into the core region is included by an empirical quantum defect μ . The quantum defect itself depends on the core structure. Once μ is determined for a number of ions with the same core structure, we can take the advantage that the quantum defect is a smooth function of $1/Z$, i.e.,

$$\mu = \frac{a}{Z} + \frac{b}{Z^2} + \frac{c}{Z^3} \quad (10)$$

for each core. As shown elsewhere, this method allows us to obtain energy levels along an isoelectronic sequence needing only a small number of calculations. It is straightforward to generalize this result to intershell states.

SUMMARY

We have shown that the approximate energy formula derived here for intrashell states allows us to obtain quite accurate energy levels of doubly excited states. A method for obtaining energies for intershell states have also been presented. By a slight modification, one can also obtain the energies of doubly excited states of multielectron atoms and ions. The formula is particularly useful along isoelectronic sequences since it affords simple extrapolations. Approximate energy levels thus obtained are useful to experimentalists for estimating the states populated in a given ion-atom collision.

References

- [1] For a recent review, see C. D. Lin, Adv. Mol. Phys. Vol. 22 (1986).
- [2] See for example, R. Mann, C. L. Cocke, A. S. Schlachter, M. Prior and R. Marrus, Phys. Rev. Lett. 49, 1329 (1982).
- [3] N. Stolterfoht, C. C. Havener, R. A. Phaneuf, J. K. Swenson, S. M. Shafroth and F. W. Meyer, Phys. Rev. Lett. 57, 74 (1986).
- [4] (a) C. D. Lin, Phys. Rev. Lett. 51, 1348 (1983); (b) Phys. Rev. A29, 1019 (1984).
- [5] S. J. Buckman, P. Hammond, F. H. Read and G. C. King, J. Phys. B16, 4039 (1983).
- [6] D. R. Herrick and O. Sinanoglu, Phys. Rev. A11, 97 (1975).
- [7] D. R. Herrick, Phys. Rev. A12, 413 (1975).
- [8] D. R. Herrick, M. E. Kellman and R. D. Poliak, Phys. Rev. A22, 1517 (1980).
- [9] M. Crane and L. Armstrong, Phys. Rev. A26, 294 (1982).

References (continued)

- [10] A. R. P. Rau, *Pramana*, 23, 297 (1984).
- [11] H. Bachau, *J. Phys.* B17, 1771 (1984).
- [12] L. Lipsky, R. Anania and M. J. Conneely, *At. Data Nucl. Data Tables*,
20, 127 (1977).

Table 1. Comparison of energy levels of doubly excited states of helium-like ions using the simple formula Eq. (5) with the results from the CI calculations by Bachau¹¹ (shown in parenthesis). All the energies are given in electron volts and are measured from the double ionization threshold. The screening σ was calculated using Eq. (6) for $1s^e$ and $1p^0$, and (7) for $1d^e$.

Charge	Energies (in eV)	
	$3(2,0)_3^+ 1s^e$	$4(3,0)_4^+ 1s^e$
Z = 5	68.21 (69.09)	38.48 (39.05)
6	99.90 (101.00)	56.37 (57.06)
7	137.75 (138.99)	77.56 (78.45)
8	181.59 (182.99)	102.34 (103.23)
9	231.47 (233.05)	130.43 (131.42)
10	287.41 (289.16)	161.91 (163.04)
	$3(1,1)_3^+ 1p^0$	$4(2,1)_4^+ 1p^0$
Z = 5	67.11 (67.48)	38.09 (38.47)
7	136.18 (136.22)	77.09 (77.60)
9	229.43 ((229.92)	129.70 (130.34)
	$3(2,0)_3^+ 1d^e$	$4(3,0)_4^+ 1d^e$
Z = 5	67.72 (68.24)	37.95 (38.83)
7	137.05 (137.74)	76.89 (78.12)
9	230.56 (231.42)	129.43 (130.99)

Table II. Energy levels of some intershell states of helium-like Boron ($Z = 5$) calculated using Eqs. (5) and (8) and the results are compared with those by Lipskey et al. (Ref. 12). Energies are measured in electron volts from the double ionization threshold.

State	Eqs. (5) and (8)	Ref. 12
$4(2,0)_3^+ 1s^e$	53.91	54.19
$5(2,0)_3^+ 1s^e$	47.76	47.96
$4(2,0)_3^+ 1d^e$	53.72	53.72
$5(2,0)_3^+ 1d^e$	47.66	47.72
$4(1,1)_3^+ 1p^0$	53.50	53.17
$4(1,1)_3^+ 1p^0$	47.57	47.39

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.