

## SPECTROSCOPY AND COLLISIONS WITH MULTIPLY CHARGED IONS

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Three areas in spectroscopy and collisions involving multiply charged ions are addressed. In the first a simple double Rydberg formula is given for estimating the approximate energy levels of intrashell doubly excited states of positive ions. In the second we discuss the calculation of alignment transfer for an electron captured to excited states and how to relate the measured polarization to the alignment of an excited state. In the last area we present some calculations on the density matrix of a hydrogenic excited manifold and other related physical quantities for the interpretation of the collision mechanisms.

### 1. Introduction

In recent years, there has been significant progress in the study of ion-atom collisions with multiply charged ions. Measurements of total charge transfer cross sections alone are no longer of extreme interest. Instead, experiments which provide more detailed information about the collision dynamics are becoming more important. Interpretations of such measurements often require additional theoretical understanding of the spectroscopy of the collision system as well as new tools of analysis. In this article I will cover three independent areas which came to my attention in the study of collisions involving multiply charged ions.

In the first area, I will address the question of estimating energy levels of doubly excited states of positive ions. It is well known that doubly excited states are easily produced in the collisions between multiply charged ions with multi-electron neutral atoms or molecules, either by double electron capture or by simultaneous excitation and capture (including both RTE and NTE). With the increasing availability of slow, highly charged heavy ions, we can expect that the spectroscopy of doubly excited states with both electrons at high principal quantum numbers be observed. It is pertinent to provide a simple formula for estimating the energy levels of these doubly excited states. Such a formula is given in section 2, together with a simple derivation and description.

In the second area, I will address questions related to the measurements of polarizations or other anisotropy parameters in ion-atom collisions. The anisotropy of the collision products can be inferred by measuring, for example, the polarization of the emitted radiation. Comparison of these measurements with theoretical predictions is often complicated by the contribution due to the cascade from higher states. We analyze how the

alignment of an upper state is transferred to a lower state, taking into consideration the spin-orbit interactions of the states involved. The method is applied to analyze some experimental data.

In the third area I will present some progress we have made on the full density matrix description of a collision event. Specifically the full  $H(n=3)$  density matrix for the charge transfer process in p-He collisions will be addressed and the results are to be compared with experiments. Derived quantities from these calculated density matrices are interpreted classically for a fuller description of the collision process.

### 2. Double Rydberg formula for the energy levels of doubly excited states of positive ions

When slow multiply charged ions collide with multi-electron atoms or molecules, multiple electron capture processes are frequently observed. These electrons usually end up at various multiply excited states of the positive ions, which are stabilized via electron emissions. These states are usually observed in energy-gain spectroscopy as "transfer ionization" peaks, or by the electron spectroscopy.

Our understanding of multiply excited states so far is quite limited. Even for doubly excited states, the energy levels of these states for most atoms are unknown. Recently we have derived a double Rydberg formula for estimating the energy levels of intrashell doubly excited states [1]. This formula is applicable to a certain class of doubly excited states when more accurate calculations are not available. It was derived using the angular correlation properties of doubly excited states and in terms of the classification scheme developed recently [2].

I start with the two-electron Hamiltonian and re-

write it as

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

where  $Z^*$  is an effective charge, and  $Z$  is the charge of the nucleus. The wave function is assumed to be a linear superposition of products of hydrogenic wave functions corresponding to a screen charge  $Z^*$ . Consider intrashell states with principal quantum number  $N$ , then

$$\left\langle \frac{1}{r_1} \right\rangle = \left\langle \frac{1}{r_2} \right\rangle = \left\langle \frac{1}{r} \right\rangle = \frac{Z^*}{N^2}. \quad (2)$$

In the CI approach, one would then evaluate the  $1/r_{12}$  integral within the subspace and then diagonalize the Hamiltonian. Here we take the advantage of the fact that for the two electrons, being at about equal distances from the core, the expectation value of  $1/r_{12}$  is proportional to  $\langle 1/r \rangle$ . By using the following approximation

$$\left\langle \frac{1}{r_{12}} \right\rangle = \left\langle \frac{1}{r} \right\rangle \frac{1}{(2 - 2\langle \cos \theta_{12} \rangle)^{1/2}} = \frac{Z^*}{N^2} (2\sigma), \quad (3)$$

where the proportionality constant  $2\sigma$  is related to the geometry of the electron pair through the average of  $\cos \theta_{12}$ . This approximation leads to the following expression for  $\langle H \rangle$ :

$$\langle H \rangle = -\frac{Z^*}{N^2} (2Z - Z^* - 2\sigma). \quad (4)$$

Setting the variation of  $\langle H \rangle$  with respect to  $Z^*$  equal to zero yields

$$\langle H \rangle = E_{N,N} = -\frac{(Z - \sigma)^2}{N^2} \text{ (a.u.)}, \quad (5)$$

which expresses the energy of each doubly excited state in terms of a screening constant  $\sigma$ . This constant is related to the average of  $\cos \theta_{12}$  for that state. A convenient approximate expression for  $\langle \cos \theta_{12} \rangle$  has been given by Herrick et al. [3] using the SO(4) group theory from which

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

The  $K$  and  $T$  quantum numbers are given under the restriction

$$\begin{aligned} T &= 0, 1, 2, \dots, \min(L, N-1), \\ K &= (N-1-T), (N-3-T), \dots, -(N-1-T); \end{aligned} \quad (7)$$

$T=0$  is not allowed if the parity of the state is  $(-1)^{L+1}$ .

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 Bachau [4] (shown in parenthesis). All the energies are given in eV and are measured from the double ionization threshold. The screening  $\sigma$  was calculated using eq. (6).

Charge $Z$	Energy (eV)
$3(2, 0)_3^+ 1S^e$	
5	68.21 (69.09)
6	99.90 (101.00)
7	137.75 (138.99)
8	181.59 (182.99)
9	231.47 (233.05)
10	287.41 (289.16)
$4(3, 0)_4^+ 1S^e$	
5	38.48 (39.05)
6	56.37 (57.06)
7	77.56 (78.45)
8	102.34 (103.23)
9	130.43 (131.42)
10	161.91 (163.04)
$3(1, 1)_3^+ 1P^o$	
5	67.11 (67.48)
7	136.18 (136.62)
9	229.43 (229.92)
$4(2, 1)_4^+ 1P^o$	
5	38.09 (38.47)
7	77.09 (77.60)
9	129.70 (130.34)
$3(2, 0)_3^+ 1D^e$	
5	67.72 (68.24)
7	137.05 (137.74)
9	230.56 (231.42)
$4(3, 0)_4^+ 1D^e$	
5	37.95 (38.83)
7	76.89 (78.12)
9	129.43 (130.99)

In fact, the analysis of doubly excited states indicates that an additional quantum number  $A = +1, -1, \text{ or } 0$  is needed. All the intrashell states have  $A = +1$ . The expression (6) is valid for states with large positive  $K$ . For smaller and negative  $K$ 's, the intrashell CI approximation is not adequate and the SO(4) expression (6) is not valid.

Using eqs. (6) and (5), we can estimate the energies of intrashell doubly excited states. In table 1, we compare the energies thus calculated with those obtained using a more extended CI method by Bachau [4]. We note that the accuracy of the simple formula is within 1%. For the purpose of estimating the energy levels of doubly excited states of positive ions, this accuracy is adequate. Using the simple curve-crossing model with

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the energy levels of doubly excited states given by eqs. (5) and (6), one can estimate which states are likely to be populated in a collision.

Without giving any details here [1], we point out that it is possible to modify eq. (5) for doubly excited states of multi-electron atoms. We have also proposed a method of estimating the energy levels of intershell doubly excited states. These details are given elsewhere [1].

### 3. Polarizations of emitted radiations following electron capture by highly charged ions

The excited states of highly charged ions populated by charge transfer are frequently aligned. The alignment of each  $nl$  level often reflects the initial alignment due to the collision as well as the alignment of higher levels which cascade down to this level. Experimental measurement of the polarization of the radiative decay of the  $nl$  level thus includes contribution from the cascades. To compare the measured results with ab initio calculations, it is necessary to entangle the cascade contributions.

We adopt the alignment transfer theory to calculate the transfer of anisotropy from a given state as it cascades to another. To compute the anisotropy transfer we take advantage of some simplifications characteristic of hydrogenic ions but often found in other ions. First, one has that the decay widths are much smaller than the fine-structure splitting. This permits one to compute anisotropy transfer between states labeled by  $LSJ$  quantum numbers. Second, we assume that Russell-Sanders coupling holds. This allows branching ratios for radiative transitions between fine-structure levels in the decay  $n_{i+1}L_{i+1} \rightarrow n_iL_i$  to be treated by standard angular momentum recoupling theory. Branching to different  $nL$  levels requires a knowledge of radial matrix elements. For hydrogenic ions the radial matrix elements and transition probabilities are available in standard references [5]. We therefore compute the anisotropy transfer for each sequence of transitions  $n_N L_N S J_N \rightarrow n_{N-1} L_{N-1} S J_{N-1} \rightarrow \cdots \rightarrow n_1 L_1 S J_1$ . We suppose that the alignment is measured by observing the angular distribution or polarization of radiation [6] emitted in the transitions  $N_1 L_1 S J_1 \rightarrow n_0 L_0 S J_0$ . In this last transition it is usually true that fine structure is not resolved so that it is necessary to sum or average over fine structure levels  $J_1$  and  $J_0$ . In addition, it is necessary to sum over all intermediate fine structure levels  $J_i$  allowed by dipole selection rules. This gives the anisotropy transfer factor for the chain  $n_N L_N \rightarrow n_{N-1} L_{N-1} \rightarrow \cdots \rightarrow n_1 L_1$ .

The derivation of the alignment transfer is given elsewhere [7]. The final expression for the alignment

transfer coefficient for the indicated chain is

$$\begin{aligned} \zeta = & \left[ \frac{(L_1 + 3/2)(L_1 - 1/2)}{L_1(L_1 + 1)} \right. \\ & \times \left. \frac{L_N(L_N + 1)}{(L_N + 3/2)(L_N - 1/2)} \right]^{1/2} \\ & \times \left[ \sum_{J_1 J_N} (-1)^{L_1 - L_N + J_1 - J_N} \frac{(2J_1 + 1)(2J_N + 1)}{(2S + 1)} \right. \\ & \times \left. \left\{ \begin{matrix} L_1 & J_1 & S \\ J_1 & L_1 & k \end{matrix} \right\} D(k, J_1 J_N) \left\{ \begin{matrix} L_N & J_N & S \\ J_N & L_N & k \end{matrix} \right\} \right] \\ & \times (2L_1 + 1)^{1/2} (2L_2 + 1) \cdots (2L_{N-1} + 1) \\ & \times (2L_N + 1)^{1/2} \end{aligned} \quad (8)$$

with  $k = 2$ , where

$$\begin{aligned} D(k, J_1 J_N) &= \sum_{J_2 J_3 \cdots J_{N-1}} B(k, J_1 J_2) \\ & \times B(k, J_2 J_3) \cdots B(k, J_{N-1} J_N), \quad N > 2 \\ D(k, J_1 J_N) &= B(k, J_1 J_2), \quad N = 2, \\ D(k, J_1 J_N) &= \delta(J_1 J_N), \quad N = 1. \end{aligned} \quad (9)$$

and

$$\begin{aligned} B(k, J_i J_{i+1}) &= (2J_{i+1} + 1)(2J_i + 1)(-1)^{J_{i+1} + J_i + 1 + k} \\ & \times \left\{ \begin{matrix} L_{i+1} & J_{i+1} & S \\ J_i & L_i & 1 \end{matrix} \right\}^2 \left\{ \begin{matrix} J_{i+1} & J_i & 1 \\ J_i & J_{i+1} & k \end{matrix} \right\}. \end{aligned} \quad (10)$$

For  $S = 0$ , the alignment transfer coefficient is very simple [7]:

$$\zeta = \frac{2L_1 - 1}{L_1 + 1} \frac{L_N + 1}{2L_N - 1}. \quad (11)$$

The results for  $S = \frac{1}{2}$  and  $S = 1$  are given in table 2.

The alignment of an excited state  $i$  is determined by the alignment of the state produced in a collision and by the transfer of alignment due to the cascade from the higher states  $j$ . To evaluate the alignment of state  $i$  we need to calculate the weighted alignment from all the possible cascade channels. Let the cross section and the alignment for state  $j$  produced by the collision by  $\sigma_j$  and  $A_0^{\text{col}}(j)$ , respectively. If the fraction of radiative transitions from state  $j$  to state  $k$  via branch  $k$  is  $\omega_k(j)$  and the alignment transfer coefficient is  $\zeta_k(j)$ , the alignment for state  $i$  is given by

$$A_0^{\text{col}}(i) = \frac{\sum_j \sum_k \omega_k(j) [\zeta_k(j) A_0^{\text{col}}(j)] \sigma_j}{\sum_j \sum_k \omega_k(j) \sigma_j}. \quad (12)$$

Once the alignment of state  $i$  is calculated, the

Table 2

Alignment transfer coefficients due to cascades and spin-orbit interactions for (a)  $S=1/2$  and (b)  $S=1$  states. The initial angular momentum of the excited state  $L_N$  is listed in the first row, the final angular momentum  $L_1$  of the excited state is listed as the first column. Only dipole transitions where the angular momentum decreases by one unit in each step are considered. For example, if  $L_N=4$ ,  $L_1=1$ , the considered cascade is  $4 \rightarrow 3 \rightarrow 2 \rightarrow 1$ . The diagonal elements reflect the average over spin-orbit interactions.

(a)  $S=1/2$ 

$L_1$	$L_N$								
	1	2	3	4	5	6	7	8	9
9									0.98338
8								0.97924	0.96196
7							0.97333	0.95170	0.93491
6						0.96450	0.93667	0.91586	0.89971
5					0.95041	0.91337	0.88705	0.86737	0.85208
4				0.92593	0.87484	0.84048	0.81631	0.79823	0.78418
3			0.87755	0.80242	0.75811	0.72877	0.70763	0.69230	0.68016
2		0.76000	0.64718	0.59296	0.56078	0.53973	0.52414	0.51269	0.50379
1	0.33333	0.24667	0.21693	0.20150	0.19150	0.18473	0.18001	0.17635	0.17346

(b)  $S=1$ 

$L_1$	$L_N$								
	1	2	3	4	5	6	7	8	9
9									0.95617
8								0.94541	0.93185
7							0.93017	0.91386	0.90076
6						0.90760	0.88777	0.87271	0.85975
5					0.87223	0.84797	0.82950	0.81502	0.80338
4				0.81253	0.78317	0.76154	0.74507	0.73174	0.72152
3			0.70153	0.66878	0.64510	0.62758	0.61418	0.60336	0.59529
2		0.47333	0.45016	0.43067	0.41645	0.40600	0.39775	0.39124	0.38594
1	0.2778	0.15056	0.13397	0.12666	0.12213	0.11894	0.11655	0.11468	0.11316

polarization can be used to compare with experimental measurement. For example the polarization of the decay of  $np$  states is given by [8]

$$P = -3A_0^{\text{col}} / (2 - A_0^{\text{col}}). \quad (13)$$

Applications of this analysis to several measurements can be found elsewhere [7].

#### 4. Density matrix for H atoms formed in electron capture process in ion-atom collisions

The density matrix formalism provides a complete characterization of collisionally produced excited states. For hydrogenic excited final states, the full density matrix within a given  $n$ -manifold can be determined experimentally by measuring four Stoke's parameters of the emitted radiation as a function of applied external axial and/or transverse electric fields. Experimentally, the full  $n=3$  density matrix of hydrogen atoms after electron capture in p-He collisions has been determined by the North Carolina State group [9] in the energy range of 40–80 keV.

The determination of the density matrix from experimental Stoke's parameters requires an elaborate numerical fitting procedure. In theoretical calculations, the density matrix is implicitly contained in the calculated scattering amplitudes. We have applied the atomic-orbital basis expansion method to p-He collisions in the 25–100 keV region to extract the  $H(n=3)$  density matrix [10]. In the energy region considered, it is essential to include some pseudostates to represent the effect of ionization channels on the electron capture processes in the close-coupling type calculations [11]. Using a basis set of the order of 20 states, we have been able to obtain reasonably converged results for the capture cross sections as well as scattering amplitudes. The calculated density matrix is compared with the experimentally determined one at 60 keV in table 3. In this table we also show the diagonal matrix elements obtained by the Harvard group [12]. From the density matrix, we have also derived an effective dipole moment and an effective velocity vector  $\langle \mathbf{L} \times \mathbf{A} \rangle$  [13]. This last quantity is equivalent to the classical orbital velocity at the perihelion. The density matrix shown in table 3 can be used to construct the charge density for the  $n=3$

Table 3

Integrated density matrix (normalized to the 3s cross section) for the  $n=3$  manifold of H atoms formed in  $H^+ + He$  collisions at 60 keV.

Element	Present	Expt. [9]	Expt. [12]
$s_0$	1.0	1.0	1.0
$s_0p_0$	$0.27 - i 0.134$	$0.30 - i 0.06$	—
$s_0d_0$	$0.11 + i 0.02$	$0.12 - i 0.47$	—
$p_0$	0.232	0.25	0.16
$p_1$	0.012	-0.01	0.06
$p_0d_0$	$0.062 + i 0.056$	$0.05 + i 0.02$	—
$p_1d_1$	$0.004 + i 0.004$	$0.01 + i 0.01$	—
$d_0$	0.03	0.01	0.011
$d_1$	0.0024	0.01	0.018
$d_2$	0.00014	0.01	-0.001
$\langle D_z \rangle$	3.62	$3.99^a$	—
$\langle L \times A \rangle_{z,s}$	0.1176	0.02	—

<sup>a)</sup> This value is with transverse field; with an axial field the value is 3.57.

manifold. These charge densities are shown in fig. 1 at 35 and 60 keV. Note that the electron cloud lags behind the projectile in both cases.

The theoretical calculation also provides impact parameter dependence of the density matrix. From the derived dipole moment  $\mathbf{D}$  and the velocity vector  $\langle \mathbf{L} \times \mathbf{A} \rangle$ , we have been able to construct a classical orbit which is consistent with the quantum mechanically calculated  $\mathbf{D}$  and  $\mathbf{L} \times \mathbf{A}$ . The orbits depend on the impact parameters. They are shown schematically in fig. 2. At large impact parameters, due to a short interaction time, we can expect that the electron is pulled towards to projectile throughout the collision time; thus the electron lags behind the projectile nucleus and lies between the two heavy particles. On the other hand, for collisions at small  $b$  values, the electron has to swing back toward the projectile as it overshoots to the right during the early stage of the collision.

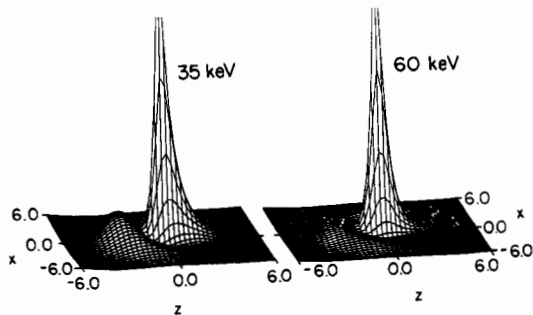


Fig. 1. Electron charge distribution of the  $H(n=3)$  manifold of states after electron capture in p-He collisions at 35 and 60 keV, respectively. The beam direction is along  $+z$ .

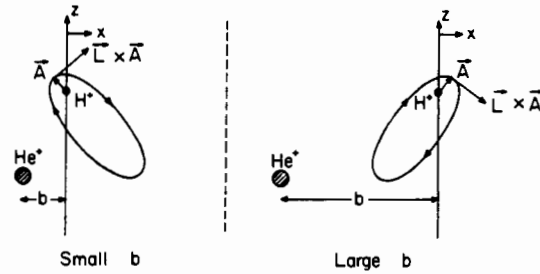


Fig. 2. A classical orbit picture of the electron after the capture in the small and large impact parameters.

We are investigating the density matrix for other systems and other energies. At present, there is no other measurements of the full density matrix for other collision systems.

## 5. Discussion

Over the past few years we have witnessed the good progress made in the study of ion-atom collisions with multiply charged ions. Interesting experiments in this area require high-resolution measurements of photons and/or electrons following the collision. These detailed studies would provide data needed for distinguishing simple models from others where the collision mechanisms can be identified. For this purpose, we have shown the analysis of polarization and/or density matrix is needed in bringing theoretical calculations directly in comparison with experiments. We have also emphasized the need for pursuing high resolution electron spectroscopy in the study of multiply excited states produced in collisions of atoms and molecules with multiply charged ions. The subject of multiply excited states is a new field where experimentalists in this area may have substantial contribution in the future.

## Acknowledgements

The works reported here are the results of collaboration with S. Watanabe (section 2), J. Macek (section 3) and A. Jain and W. Fritsch (section 4). Without their contributions, it would be impossible to present these results here. I also acknowledge the support by the National Science Council of Taiwan under grant number NSC76-0208-M001-41 and by the US Department of Energy, Office of Energy Research, Division of Chemical Sciences.

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