

# Detailed atomic structure of neutral and near-neutral systems

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# Structure of the talk

- Motivational material
- Underlying theory – summary
- Transitions in Sn I
- Transitions in Sn II

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# Sn I and Sn II

Tin can be used as a diagnostic tool in monitoring the erosion of vessel wall tiles in fusion plasmas, eg, ITER. (see Foster *et al* J. Nucl. Mat. **363-5**, 152, 2006).

Key transitions are in Sn I and Sn II in the range  
 $\lambda\lambda$  4500 – 5600 Å

The abundance of tin in the ISM is determined from the 5p–5d transition in Sn II at 1400Å. On the basis of an experimental oscillator strength, the abundance appears to be super-solar. Recent theory gives a larger value, leading to a reduction of the abundance.

## Lines of interest

Obs (Å)	NIST	$\Delta E$ ( $\text{cm}^{-1}$ )	Transition	
4587		21801		
5333	5332	18751	$6p^2 P_{1/2}^o \rightarrow 6d^2 D_{3/2}$	Sn II
5358		18692		
5370		18622		
5393		18543		
5424		18437		
5444		18369		
5458		18322		
5545		18034		
5583	5588	17912	$5d^2 D_{3/2} \rightarrow 4f^2 F_{5/2}^o$	Sn II

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# CI wave functions

In LSJ coupling, CI wave functions take the form

$$\Psi(J) = \sum_{i=1}^M a_i \Phi_i(L_i S_i J)$$

For a given set of Configuration State Functions (CSFs)  $\{\Phi_i\}$ , the optimal values of the CI coefficients  $\{a_i\}$  are the eigenvector components of the Hamiltonian matrix with typical element  $\langle \Phi_i | H | \Phi_j \rangle$ , and the calculated energies are the corresponding eigenvalues. It is customary (but not always appropriate) to label each wave function by the CSF with the largest component in the eigenvector.

The CSFs are constructed from one-electron orbitals:

$$u_i(\mathbf{r}, \sigma) = \frac{1}{r} P_{n_i l_i}(r) Y_{l_i}^{m_{l_i}}(\theta, \phi) \chi_{m_s}(\sigma)$$

and of these, the radial functions  $P_{n_i l_i}(r)$  remain to be chosen.

Because of the Hylleraas-Undheim theorem, the energy eigenvalues satisfy the variational principles

$$E^{(i)} \geq E_{\text{exact}}^{(i)}$$

Hence the radial functions can be optimised to make any particular eigenvalue as low (negative) as possible.



# Difficulties encountered

- The electron occupancy specified in the labels of many levels may be the same, but the optimal radial functions of the orbitals maybe (very) different.
- Electron correlation, introduced through CI, may change different level energies by different amounts.
- Calculated differences between energy levels will not be as accurate as experimental values.
- The CI expansions of the wave functions, and thus of any other atomic property, are slowly convergent.

# How can we improve accuracy?

- Increase the number of CSFs and orbitals *systematically*.
- Examine the convergence of the results and apply extrapolation methods, for example by ‘fine-tuning’:  
make small adjustments to the diagonal (and off-diagonal) Hamiltonian matrix elements so that the eigenvalue differences agree with experimental energy differences.
- Compare with laboratory experiments and astrophysical observations.

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## Source of material

- Paul Oliver and Alan Hibbert  
J Phys B **41** 165003 (2008)
- Paul Oliver, PhD thesis, QUB (2008)

# Nature of the calculation

States to be considered:

$$[1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}] 5s^2 5p^2, 5s 5p^3, \\ 5s^2 5pnl \quad (nl = 6s, 7s, 6p, 7p, 5d, 6d, 4f, 5f).$$

Types of correlation effects included:

- Ground state Hartree-Fock functions ( $1s \rightarrow 5p$ )
- Functions describing the outer electron ( $nl$ )
- Valence-shell correlation
- ‘Correcting’ orbitals: different orbitals for different  $LS$
- Core polarisation, explicitly with CI:  $4d \rightarrow nf$

# Nature of the calculation

Orbital included:

- $ns, n = 1 \rightarrow 10$
- $np, n = 2 \rightarrow 11$
- $nd, n = 3 \rightarrow 11$
- $nf, n = 4 \rightarrow 11$
- $ng, n = 5 \rightarrow 7$
- $nh, n = 6, 7$

## Some LS oscillator strengths

Transition	Calc 1		Calc 2		Calc 3	
	$f_l$	$f_v$	$f_l$	$f_v$	$f_l$	$f_v$
$5p^2\ ^3P - 6s\ ^3P^o$	0.261	0.253	0.260	0.252	0.259	0.244
$5p^2\ ^3P - 5d\ ^3P^o$	0.099	0.087	0.097	0.087	0.096	0.092
$5p^2\ ^1D - 5d\ ^1D^o$	0.089	0.089	0.085	0.085	0.075	0.069
$5p^2\ ^1S - 6s\ ^1P^o$	0.085	0.092	0.087	0.090	0.083	0.072
$5p^2\ ^1S - 5d\ ^1P^o$	0.738	0.697	0.485	0.499	0.467	0.446
$6p\ ^3P - 6s\ ^3P^o$	0.434	0.405	0.447	0.398	0.444	0.424
$6p\ ^3P - 5d\ ^3P^o$	0.062	0.085	0.058	0.076	0.044	0.045
$6p\ ^3S - 6s\ ^3P^o$	0.124	0.124	0.125	0.122	0.124	0.119
$6p\ ^3S - 5d\ ^3P^o$	0.215	0.400	0.209	0.357	0.158	0.172
$6p\ ^1S - 6s\ ^1P^o$	0.077	0.113	0.081	0.096	0.086	0.080
$6p\ ^1S - 5d\ ^1P^o$	0.226	0.083	0.310	0.206	0.317	0.284
$4f\ ^1D - 5d\ ^1D^o$	0.074	0.057	0.075	0.056	0.041	0.041

# Size of the LSJ calculation

## Number of CSFs

J	Odd	Even
0.5	11201	10504
1.5	33850	29809
2.5	49697	36722
3.5	43919	25456
4.5	25800	8793
5.5	9098	



## Some radiative lifetimes (ns)

Level	Theory		Experiment			
	Present	[1]	[2]	[3]	[4]	[5]
$5p6s\ ^3P_0$	5.23	4.8	$6.0\pm 0.9$			$5.7\pm 0.6$
$5p6s\ ^3P_1$	5.02	4.8	$6.0\pm 0.9$	$4.75\pm 0.18$	$4.2\pm 0.4$	$5.0\pm 0.5$
$5p6s\ ^3P_2$	4.61	4.6	$4.7\pm 0.7$	$4.25\pm 0.23$	$4.3\pm 0.5$	$4.6\pm 0.5$
$5p6s\ ^1P_1$	4.48	4.2		$4.11\pm 0.22$	$5.4\pm 0.5$	$4.4\pm 0.5$
$5p5d\ ^3D_1$	4.09			$3.9\pm 0.5$	$4.5\pm 0.5$	$5.5\pm 0.6$
$5p5d\ ^3D_2$	6.23			$5.5\pm 0.4$		$6.8\pm 0.7$
$5p5d\ ^3D_3$	7.90				$6.5\pm 1.0$	$6.0\pm 0.6$
$5p5d\ ^1D_2$	18.05					$24\pm 2$
$5p5d\ ^3F_3$	6.78			$5.8\pm 0.6$		$6.9\pm 0.7$

[1]: Migdalek (1979); [2]: Lawrence (1967); [3]: Holmgren & Svanberg (1972);  
 [4]: Andersen et al (1972); [5]: Gorshkov & Verolainen (1985)

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- Paul Oliver and Alan Hibbert  
J Phys B **43** 074013 (2010)
- Paul Oliver, PhD thesis, QUB (2008)

# Transitions of particular interest

$\lambda(\text{\AA})$	transition
1400.5	$5p^2 P_{0.5}^o - 5d^2 D_{1.5}$
1489.1	$5p^2 P_{1.5}^o - 5d^2 D_{1.5}$
1475.0	$5p^2 P_{1.5}^o - 5d^2 D_{2.5}$
5591.0	$5d^2 D_{1.5} - 4f^2 D_{2.5}^o$
5333.9	$6p^2 P_{0.5}^o - 6d^2 D_{1.5}$
5562.7	$6d^2 P_{1.5}^o - 6d^2 D_{2.5}$

# Orbitals and CSF sets used at different stages of complexity of the calculation

Calc.	Orbitals	CSF sets	
1	$1s \rightarrow 5p, 6s,$ $6p, 5d, 6d, 4f$	$5s^2 nl (nl = 5p, 6p, 4f)$	$5s5p^2$ $5s^2 nl (nl = 6s, 5d, 6d)$
2	$+ 7s, 5f, 7p, 7d$	1- and 2-electron replacements from reference sets comprising the configuration sets of calculation 1, retaining a $4d^{10}$ core	
3	$+ 6f, 8p, 7f, 5g,$ $8s, 6g$	1- and 2-electron replacements from reference sets in 2, retaining up to $4p^6$ in the core	
4	As in 3	1- and 2-electron replacements from reference sets in 2, retaining up to $4s^2$ in the core	
5	$+ 9p, 9s, 10s,$ $8d, 10p$	1- and 2-electron replacements from reference sets in 2, but retaining $4p^6$ in the core	
6	As in 5	1- and 2-electron replacements from the multi-reference configuration sets in the following table, (retaining $4p^6$ in the core)	

## Multi-reference set for the final calculation

$LS\pi$	Reference Configurations	$LS\pi$	Reference Configurations
$^2P^o$	$5s^2np(5 \leq n \leq 10)$ $5p^2np(5 \leq n \leq 8, 10p)$	$^2D$	$5s5p^2$ $5s^2nd(5 \leq n \leq 8)$ $5p^2nd(5 \leq n \leq 8)$
$^2F^o$	$5s^24f$ $5p^24f$		$5smsnd(m = 6, 7; 5 \leq n \leq 8)$ $5s5p5f$
$^2S$	$5s5p^2$ $5s5d^2$ $5s^2ns(6 \leq n \leq 10)$ $5p^2ns(6 \leq n \leq 8, 10s)$	$^4P$	$5p^2nl(nl = ms, (5 \leq m \leq 7), 5d)$ $5s5d^2$ $5s5pnp(n = 6, 7)$
$^2P$	$5s5p^2$ $5p^25d$		

# CI mixing coefficients $a^2(\%)$ for the strongly-interacting **A=5s5p<sup>2</sup>** and **B=5s<sup>2</sup>5d<sup>2</sup>D** states.

Calc.	$\Delta E_{\text{sep}}$	State	$\Delta E_{\text{trans}}$	$a^2(\text{A})$	$a^2(\text{B})$	$f_l$	$f_v$
1	22889	5s5p <sup>2</sup> <sup>2</sup> D	44396	72	28	0.0114	0.0004
		5s <sup>2</sup> 5d <sup>2</sup> <sup>2</sup> D	67285	22	77	1.4940	0.8769
2	15514	5s5p <sup>2</sup> <sup>2</sup> D	53253	57	39	0.0072	0.0039
		5s <sup>2</sup> 5d <sup>2</sup> <sup>2</sup> D	68767	33	58	1.2017	1.1363
3	13204	5s5p <sup>2</sup> <sup>2</sup> D	54945	50	44	0.0301	0.0291
		5s <sup>2</sup> 5d <sup>2</sup> <sup>2</sup> D	68149	40	52	1.1129	1.0466
4	13167	5s5p <sup>2</sup> <sup>2</sup> D	54829	50	43	0.0297	0.0325
		5s <sup>2</sup> 5d <sup>2</sup> <sup>2</sup> D	67996	40	52	1.1143	1.0312
5	12989	5s5p <sup>2</sup> <sup>2</sup> D	55198	49	44	0.0333	0.0371
		5s <sup>2</sup> 5d <sup>2</sup> <sup>2</sup> D	68187	40	51	1.1004	1.0229
6	12887	5s5p <sup>2</sup> <sup>2</sup> D	55512	48	45	0.0408	0.0367
		5s <sup>2</sup> 5d <sup>2</sup> <sup>2</sup> D	68399	42	49	1.0775	1.0606
Expt.	12576	5s5p <sup>2</sup> <sup>2</sup> D	56381				
		5s <sup>2</sup> 5d <sup>2</sup> <sup>2</sup> D	68957				

## Comparison of oscillator strengths

Lower	Upper	$\lambda(\text{\AA})$	This work			Experiment		
			$f_l$	$f_v$	HFR	BFS	APE	LPP
$5p^2 P_{0.5}^o$	$5d^2 D_{1.5}$	1400.5	1.205	1.151	1.25	1.04{5}		
$5p^2 P_{1.5}^o$	$5d^2 D_{1.5}$	1489.1	0.053	0.048	0.105	0.170{14}		
$5p^2 P_{1.5}^o$	$5d^2 D_{2.5}$	1475.0	0.952	0.945	0.970	1.06{9}		
$5d^2 D_{1.5}$	$4f^2 F_{2.5}^o$	5591.0	0.545	0.541	0.408	0.51	0.595	0.478
$6p^2 P_{0.5}^o$	$6d^2 D_{1.5}$	5333.9	0.841	0.818	0.930		0.733	0.495
$6p^2 P_{1.5}^o$	$6d^2 D_{2.5}$	5562.7	0.788	0.778	0.800		0.821	0.633

### Notes:

HFR: Relativistic HF + CI, Alonso-Medina et al, Phys Scr **71** 154 (2005)

BFS: Beam-foil spectroscopy, Schectman et al, ApJ **542** 400 (2000)

APE: Arc plasma emission spectroscopy, Wujec & Weniger, JQSRT, **18** 50 (1977)

LPP: Laser produced plasmas, Alonso-Medina & Col3n, Phys Scr **61** 646 (2000)



## The abundance of tin in the ISM

- The solar abundance (ratio) of tin is:  $\log(\text{Sn}/\text{H}) = -9.86 \pm 0.04$ . (Grevesse & Noels, 1996).
- Sofia et al, ApJ **522** L137 (1999), used the GHRS on HST to study the ISM in the direction of 14 stars. They find that the ISM abundance ratio **exceeds** that of the Sun by
  - $0.07 \pm 0.04$  dex, if sight lines with  $\log f(\text{H}_2) \leq -3.0$  are included;
  - $0.04 \pm 0.02$  dex, if sight lines with  $\log f(\text{H}_2) \leq -1.0$  are also included;where  $f(\text{H}_2)$  is the fraction of molecular hydrogen, assuming the oscillator strength of the  $1400.5\text{\AA}$  line is 1.04 (Schectman et al).
- If our value of 1.205 is use instead, the abundance ratio is reduced by  $-0.064$  dex, so that the abundance of tin is close to that of the Sun.

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5370		18622	?	
5393		18543	?	
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5444		18369	?	
5458		18322	?	
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5583	5588	17912	$5d^2 D_{3/2} \rightarrow 4f^2 F_{5/2}^o$	Sn II