Elements of the Periodic Table

1. The rich cowboy on the white horse always says “Hi, Yo Ag.
2. Hg is a brand of automobile.
3. A prisoner who is always fooling around is known as a Si.
4. After many failures, Edison still B.
5. Two nickels are worth Sn cents.
6. What do I make a week? Fe $200 per week.
7. If you get robbed, call a Cu.
8. A female relative whose name spells dollars Sb.
9. If you fail to do your school work, your marks will S or Zn.
10. When he contracted a disease, the doctor said he could Cm.
11. When he broke his leg the doctor said he could He.
12. If no one answers the door, surely they Ar.
13. If you catch a robber in the act use your Ne him.
14. The fat man carefully Kr the thin ice.
15. I bought a new horse the other day and Rh home.
16. We’ve come to praise Cs not Ba.
17. If you’ve been bad, St. Ni will skip your house at Xmas.
18. An Olympic slogan is “Go for the Au”
19. The nosy couple were asked mind their own Bi.
20. The rebels conducted a Rn the supply store.
General form of the electrostatic interaction in 2-electron atoms

1st order energy change is

\[ \Delta E = \left\langle \psi \left| \frac{K e^2}{|r_1 - r_2|} \right| \psi \right\rangle, \]

(where K = 1/4\(\varepsilon_0\))

Using the symmetrized wavefunctions

\[ \Delta E = \frac{1}{2} \int \,dr_1 \int \,dr_2 [u^*_n_1(r_1)u^*_n_2(r_2) \pm u^*_n_1(r_2)u^*_n_2(r_1)] \]
\[ \times \frac{K e^2}{|r_1 - r_2|} [u_{n_1}(r_1)u_{n_2}(r_2) \pm u_{n_1}(r_2)u_{n_2}(r_1)]. \]

which becomes

\[ \Delta E = \int \,dr_1 \int \,dr_2 u^*_n_1(r_1)u^*_n_2(r_2) \frac{K e^2}{|r_1 - r_2|} u_{n_1}(r_1)u_{n_2}(r_2) \]
\[ \pm \int \,dr_1 \int \,dr_2 u^*_n_1(r_1)u^*_n_2(r_2) \frac{K e^2}{|r_1 - r_2|} u_{n_1}(r_2)u_{n_2}(r_1). \]

And expanding...
- To make everything central

\[ \frac{1}{|r_1 - r_2|} = \sum_{k=0}^{\infty} \frac{r_1^k}{r_2^{k+1}} P_k(\cos \theta). \]
The Slater Integrals

From the properties of spherical harmonics, there are only small numbers of terms surviving the ANGULAR integrals – basically the triangle rule for angular momentum addition.

Hence, this infinite sum has only a few (1-4) terms for each given SLJ-state:

Each term is a direct or exchange integral, \[ E = \sum(k) \left( f_k F^k \pm g_k G^k \right) \]
Where the factor \( k = 0, 1, 2, \) etc
NB the superscripts are not powers, the \( f_k \) and \( g_k \) are the angular integrals

\[ F^k \equiv K e^2 \int dr_1 r_1^2 \int dr_2 r_2^2 |R_{n_1, \ell_1}(r_1) R_{n_2, \ell_2}(r_2)|^2 \frac{r_<^k}{r_>^{k+1}}, \]

\[ G^k \equiv K e^2 \int dr_1 r_1^2 \int dr_2 r_2^2 R_{n_1, \ell_1}(r_1) R_{n_2, \ell_2}(r_1) R_{n_1, \ell_1}(r_2) R_{n_2, \ell_2}(r_2) \frac{r_<^k}{r_>^{k+1}}. \]
Generalizing the spin-orbit interactions

In hydrogen, we found

\[ \Delta E = (g_e - 1) \frac{\hbar^2}{2m^2c^2} K Z e^2 \left\langle \frac{1 \cdot s}{r^3} \right\rangle. \]

In a general potential \( V \)
(let \( g_e = 2 \))

Define the radial part:

\[ \Delta E = \frac{\hbar^2}{2m^2c^2} \left( \frac{1}{r} \frac{dV}{dr} 1 \cdot s \right) \]

And the angular part is

\[ 1 \cdot s = \frac{j(j+1) - \ell(\ell + 1) - 3/4}{2}. \]
\[ = \frac{\ell}{2} \quad (j = \ell + 1/2) \]
\[ = -\frac{\ell}{2} \quad (j = \ell - 1/2). \]

The difference in spin-orbit energies of 2 levels is \( 2\ell + 1 \), so we introduce a spin orbit parameter \( \zeta \)

\[ \zeta_\ell \equiv \left\langle \xi \right\rangle (2\ell + 1). \]
Example of an sp configuration (e.g. helium 1s2p or nsnp)

Add the (mainly from exchange) electrostatic interactions and the spin-orbit interactions.

\[ E = E_0 + \sum(k) \left( a_k F^k + b_k G^k \right) + \sum(i) \zeta_i \]

Where the summations are taken over all states within a given configuration.

**Note** that for light atoms (e.g. helium) the spin-orbit corrections are much smaller than the electrostatic exchange energies – **DISCUSS**

For heavier atoms this becomes less so – let’s look at the example of the nsnp configurations

1. How many states are there?
2. How do we label them – spectroscopically.
3. How many terms are there in the above summations?
Solutions for the nsnp configurations

Only terms (parameters) are $F^0$, $G^1$ and $\zeta(l=1)$
Define $F_k, G_k = F^k/D_k, G^k/D_k$
Then $D_0 = 1$, and $D_1 = 3$;
and $F_0 = E_0$ (same for all states of the configuration).

<table>
<thead>
<tr>
<th></th>
<th>$^3P_0^o$</th>
<th>$^3P_1^o$</th>
<th>$^3P_2^o$</th>
<th>$^1P_1^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3P_0^o$</td>
<td>$E_0 - G_1 - \zeta_{p}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^3P_1^o$</td>
<td>0</td>
<td>$E_0 - G_1 - \zeta_{p}/2$</td>
<td>0</td>
<td>$\zeta_{p}/\sqrt{2}$</td>
</tr>
<tr>
<td>$^3P_2^o$</td>
<td>0</td>
<td>0</td>
<td>$E_0 - G_1 + \zeta_{p}/2$</td>
<td>0</td>
</tr>
<tr>
<td>$^1P_1^o$</td>
<td>0</td>
<td>$\zeta_{p}/\sqrt{2}$</td>
<td>0</td>
<td>$E_0 + G_1$</td>
</tr>
</tbody>
</table>

Note the off-diagonal matrix element between the two $J=1$ states of the spin-orbit interaction – if the electrostatic energy gap ($G_1$) between these two states is large, then this interaction can be neglected.

OK for light atoms like helium, but not for heavy atoms….
Define $x = (3\zeta_p/4)/\{G_1 + 3\zeta_p/4\}$ \hspace{1cm} $y = (E - E_0 + \zeta_p/4)/\{G_1 + 3\zeta_p/4\}$

($x$ is the fractional S-O part, $y$ is a revised energy scale)

Notes:
1. in light atoms, singlets and triplets are far apart;
2. in heavy atoms, we see 2 doublets;
3. sp and sp$^5$ (1 electron, 1 hole) configurations behave similarly;
4. We need a different coupling scheme to describe the heavier atoms.

The “jj coupling scheme”

![Diagram](image_url)
Energy level diagram of Beryllium

The Same?

Different?

How is it different?

Why is it different?
Energy level diagram of Beryllium

Notes:
1. Similar to He
2. No deep ground state.
(IP is small)
3. Singlets & triplets
4. “Displaced terms”
The Angular integrals of the Electrostatic interaction

We need to evaluate:

\[ \langle nln'l'LSJM \mid \frac{e^2}{4\pi\varepsilon_0 r_{12}} \mid nln'l'LSJM \rangle = \sum_k \left( f_k F^k + (-1)^s g_k G^k \right), \]

giving

\[ f_k = (-1)^{l+l'+L} \begin{pmatrix} l & l' & L \\ l & l' & k \end{pmatrix} \langle l||C^k||l\rangle \langle l'||C^k||l'\rangle, \]

\[ g_k = \begin{pmatrix} l & l' & L \\ l & l' & k \end{pmatrix} \langle l||C^k||l'\rangle^2. \]

Where \( C_k \) are Clebsch-Gordan coefficients, and \{\ldots\} are 6-j symbols

\[ \langle l||C^k||l'\rangle = (-1)^l \sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \]

\( \ldots \) and the \( (\ldots) \) is a 3-j symbol

The results are whole numbers or simple fractions for each \( f_k, g_k \).
Other states in helium??

We have said all helium states are of the type $1s\!\!n/1,3L_J$

with $J=L$ for singlets, $J = L-1, L, L+1$ for triplets

If we excite the “core electron” we get “displaced terms”
(seen in Be)

or “doubly-excited” states…..

Questions:
1. Where are these states in the energy level diagram for helium
2. Do they exist, and/or have they been seen?
3. What happens in a 3-electron system (lithium, etc)
4. What happens in a 4- electron system (beryllium, etc)
Fig. 1. Extreme ultraviolet spectra showing discrete anomalies in the photoionization continuum absorption of He, Ne, and Ar (increased blackness indicates increased absorption). The anomalies in the He absorption spectrum (top) are due to the mixing of two-electron excitation states with the continuum. In Ar (bottom) this mixing results in discrete windows in the absorption continuum.

Fig. 2. Densitometer trace of the absorption spectrum of He as shown in Fig. 1 (top). The anomalies are of the Beutler-Fano shape. The absorption is enhanced on the low-frequency side and reduced on the high-frequency side.

The first member of the series (60.1 eV) can be associated with the lowest allowed transition to a two-electron excitation level, namely, $1s^22s^21S_0 - 2s^22p^1P_1$. The exact position of this level can be theoretically predicted only after an evaluation of the mixing of this state with the neighboring configurations.

There are two series of energy levels important...
Autoionization Continuum states,

Consider the autoionization process as an internal re-arrangement of the atomic wavefunction, with no change of energy, angular momentum or spin:

Then (a) no changes in overall quantum numbers can occur (b) it is not a single electron process. Thus, the total angular momentum and parity do not change

\[ \Delta J = 0 \quad \Delta \pi = 0 \]

and in L-S coupling where L and S are good quantum numbers \( \Delta L = \Delta S = 0 \)

Breakdowns in LS coupling \( \rightarrow \) low rates of electron emission (could compete with normal radiative processes)

\[ \rightarrow \text{Quantum character of continuum states} \]
\[ \rightarrow \text{E.g. in helium,} \quad s, \, d.. \text{ Continua have even parity,} \]
\[ \text{p, f ...Continua have odd parity.} \]

\[ \rightarrow \text{The reverse process of radiationless capture (important in astrophysics)} \]

\[ \rightarrow \text{Helium example...} \]
Overview of **ALL** helium energy levels
The lowest doubly-excited state can be $2s2p$ or $2p2s$ singlet or triplet state. Hence use a linear combination.

\[ \psi(2n^2) = \frac{u(2snp) \pm u(2pns)}{\sqrt{2}}. \] \hspace{1cm} (1)

Indeed, a calculation with screened hydrogenic wave functions shows that the electron interaction matrix element $(2s3p | V | 2p3s) \sim 1 \text{ eV}$, whereas $E_{2s3p} - E_{2p3s} \sim 0.1 \text{ eV}$.

(a) The $+(-)$ quantum number corresponds to radial motions of the two electrons in (out of) step with one another.

(b) The $2s2p$ state belongs to the $+ \text{ classification}$.

(c) The $+ \text{ level of each pair lies presumably above the } - \text{ level}$.

(d) The optical transition from $1s^2$ to the $- \text{ level}$ is quasi-forbidden.

(e) The radiationless transition from the $+$ levels to the $1snp$ continuum is quasi-forbidden.

(f) The radiationless transition from the $-$ levels is also quasi-forbidden, by the same mechanism that leads to (d).

Dominance of $1/r_{12}$ interaction

Considering only the $^1P$ states: (photons couple only from $^1S$ to $^1P$ states)

An important physical picture of the wavefunctions.
Helium states which do not decay to the ground state

(a) States which decay to singly-excited states:
(vacuum uv transitions 30 nm region)
He+ Lyman alpha

** transition

100 keV

He II 303.8 Å

He I 309.1 Å

He I 304.5 Å

He I 302.3 Å

He I 295.2 Å

He I 294.1 Å

He I 344.7 Å

He I 338.1 Å

He I 320.3 Å

He I 314.6 Å

Counts/20 µC

Fig. 5. A beam-foil excited helium spectrum in the far ultraviolet. The transitions are all from non-autoionizing doubly-excited states except for the lyman α transition of He II at 303.8 Å [54].
An Example Experimental Arrangement
FIG. 1. Beam-foil spectrum of 150-keV He\(^+\) ions incident on a 5-\(\mu\)g/cm\(^2\) carbon foil. The solid bar indicates members of the He\(\text{II} 3\,d-nf\) series, while the arrows indicate He\(\text{I}\) doubly excited triplet transitions. Note the change of intensity scale above 2550 \(\text{Å}\).

**In lithium**, once one electron is excited from the 1s shell, all 3 electrons can have their spins aligned!

-> stable quartet states…

Can you write down and justify which states are likely to be stable? (doublets & quartets!)
Examples of observed transitions....
1 - Isoelectronic sequences – Helium, lithium

2 - Negative lithium

3 - Methods of excitation……..

4 – Lifetimes……..(by photon, electron emission)

5 – Other alkali isoelectronic sequences
Radiation from the Negative Lithium Ion

Argonne National Laboratory, Argonne, Illinois 60439
(Received 16 July 1980)

It is confirmed that the 3489-Å transition observed in beam-foil excited lithium spectra originates from the negative lithium ion. It is most probably the transition $1s2s2p^3S^0 - 1s2p^3P$, as suggested by Bunge. A new electric field acceleration technique provides identification of the charge state of the emitting ion. The decay curve is a cascade-free single exponential. The polarization and beam energy dependence of the light yield have also been measured. The transition has been identified in heavier isoelectronic ions.
DISTANCE DOWNBEAM (mm)

INTENSITY DIFFERENCE

\[ \frac{[I(V) - I(-V)]}{I(0)} \]

FIELD PLATE
(±4.75 kV)

DISTANCE DOWNBEAM (mm)
The **ONLY** light ever observed from a negative ion
All are 4-electron atoms

TABLE I. Wavelengths of the $1s2s2p^{25}P - 1s2p^{35}S^0$ transition. The experimental precision is $\pm 1 \text{ Å}$.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Theory (Å)</th>
<th>Experiment (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^-$</td>
<td>$3489^a$</td>
<td>$3489^c$</td>
</tr>
<tr>
<td>Be I</td>
<td>$1821^b$</td>
<td>$1909^c$</td>
</tr>
<tr>
<td>B II</td>
<td>$1279^b$</td>
<td>$1324.5^d$</td>
</tr>
<tr>
<td>C III</td>
<td>$989^b$</td>
<td>$1015.6^e$</td>
</tr>
<tr>
<td>N IV</td>
<td>$807^b$</td>
<td>$825^e$</td>
</tr>
<tr>
<td>O V</td>
<td>$682^b$</td>
<td>$695^e$</td>
</tr>
<tr>
<td>F VI</td>
<td>$589^b$</td>
<td>$597^f$</td>
</tr>
<tr>
<td>Ne VII</td>
<td>$519^b$</td>
<td>$\ldots$</td>
</tr>
</tbody>
</table>
How to excite highly excited states

1\textsuperscript{st} impact → excites (or ionizes) one electron
2\textsuperscript{nd} impact → excites (or ionizes) one electron
3\textsuperscript{rd} impact.....

Between impacts, the excited state might decay to the ground state

What happens for fast ions in solids?
What happens in EBIT?
DECAY OF $^{4}P_{5/2}^{0}$ AUTOIONIZING STATES OF IONS IN THE Li ISOELECTRONIC SEQUENCE

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Received 13 May 1974
Revised manuscript received 7 June 1974

Dirac-Hartree-Fock calculations of the M2 radiative decay rates and of the autoionization rates for metastable states of the Li-sequence (Z = 3 to 26) are presented. The calculations are compared with experimental determinations.
Fig. 1. The metastable decay rate plotted as a function of nuclear charge is compared with experimental data. The data marked by Δ and the associated error bars are as reported in the second paper of ref. [1].
Differential metastability of fine structure levels

Fine structure of the $1s2s2p\,^4P^o$ and $1s2p^2\,^4P$ doubly excited states in lithiumlike carbon, nitrogen, and oxygen

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(Received 30 January 1978)

The fine structure of the $1s2s2p\,^4P^o-1s2p^2\,^4P$ multiplet in the doubly excited quartet system of three-electron C IV, N v, and O vi has been measured using the method of beam-foil spectroscopy. The fine-structure splittings have been determined to within $\sim 5$ cm$^{-1}$ in both the upper and lower states of each ion, and the absolute transition wavelengths have been measured to within $\sim 0.1$ Å ($\sim 10^{-3}$ eV). The wavelength results show that existing relativistic and nonrelativistic energy separations calculated for these $^4P$ states are inaccurate by $\sim 1\%$ for $Z = 6-8$, and that calculations of the fine-structure splittings are inaccurate by (10–20)\% for $1s2s2p\,^4P^o$ and by $\geq 20\%$ for $1s2p^2\,^4P$. Lifetimes have also been measured for the $J = 5/2$, 3/2, and 1/2 levels of $1s2p^2\,^4P$. Differential metastability is found to be a characteristic feature of these core-excited fine-structure states in all three ions. Comparison with calculated autoionization and K x-ray transition rates for $Z = 7$ and 8 indicates that the $1s2p^2\,^4P_{5/2}$ lifetime is determined essentially by its autoionization rate to the doublet continuum through magnetic interactions, whereas the $J = 3/2$ and 1/2 states decay at a slower rate that is more characteristic of the $^4P^o-^4P$ radiative transition rate.
FIG. 1. Wavelength scans showing resolved fine structure of the $1s^2 2s 2p^5 \, ^3P_0 - 1s^2 2p^5 \, ^1P_1$ transition in the beam-foil spectra of C IV, N V, and O VI. The observed linewidth (FWHM) is about 0.3 Å.
Comparison of expt and theory for fine structure

TABLE II. Fine-structure intervals in the $1s2s2p^4P^0$ and $1s2p^24P$ configurations of C iv, N v, and O vi.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Levels</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Interval (cm⁻¹)</th>
<th>a</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>O vi</td>
<td>$\frac{5}{2} - \frac{3}{2}$</td>
<td>418 ± 4</td>
<td>374</td>
<td>302</td>
<td>396</td>
<td>252 ± 4</td>
<td>68</td>
<td>232</td>
</tr>
<tr>
<td></td>
<td>$\frac{3}{2} - \frac{1}{2}$</td>
<td>102 ± 5</td>
<td>86</td>
<td>-19</td>
<td>90</td>
<td>295 ± 5</td>
<td>251</td>
<td>292</td>
</tr>
<tr>
<td>N v</td>
<td>$\frac{5}{2} - \frac{3}{2}$</td>
<td>212 ± 3</td>
<td>191</td>
<td>133</td>
<td>203</td>
<td>115 ± 3</td>
<td>-24</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td>$\frac{3}{2} - \frac{1}{2}$</td>
<td>35 ± 4</td>
<td>25</td>
<td>-55</td>
<td>29</td>
<td>160 ± 4</td>
<td>126</td>
<td>156</td>
</tr>
<tr>
<td>C iv</td>
<td>$\frac{5}{2} - \frac{3}{2}$</td>
<td>100 ± 5</td>
<td>89</td>
<td>40</td>
<td>91</td>
<td>41 ± 5</td>
<td>-59</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>$\frac{3}{2} - \frac{1}{2}$</td>
<td>0 ± 7</td>
<td>-3</td>
<td>-61</td>
<td>0.9</td>
<td>83 ± 7</td>
<td>53</td>
<td>74</td>
</tr>
</tbody>
</table>

*a* Present work.

*b* Hartree–Fock (Ref. 23).

*c* Relativistic $Z$-expansion (Ref. 11).

*d* Dirac–Hartree–Fock (Ref. 33, see *Note added*).
Note: Spin-orbit, spin-other orbit and spin-spin magnetic interactions all important –

Thus, NOT Lande intervals...

FIG. 3. Experimental relative fine-structure levels of the $1s2s2p^4P^0$ and $1s2p^24P$ states in C iv, N v, and O vi determined from the present work. Also plotted are the experimental fine structures of the $1s2p^3p^0$ states in C iv (Ref. 24), N v i (Ref. 25), and O vi (Ref. 26).
TABLE III. Lifetimes of the fine-structure levels of the 1s2p^2^4^P state in C IV, N v, and O vi.

<table>
<thead>
<tr>
<th>Ion</th>
<th>J</th>
<th>Lifetime (ns.)</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>O vi</td>
<td>5/2</td>
<td>0.10 ± 0.01</td>
<td>0.11</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>1.1 ± 0.1</td>
<td>0.67</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>1.0 ± 0.1</td>
<td>18</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>N v</td>
<td>5/2</td>
<td>0.30 ± 0.05</td>
<td>0.30</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>1.7 ± 0.1</td>
<td>1.8</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>1.4 ± 0.1</td>
<td>61</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>C IV</td>
<td>5/2</td>
<td>0.9 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2</td>
<td>2.5 ± 0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>...</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a Present work.
^b Hartree–Fock–Slater (Ref. 15).
^c Hartree–Fock–Slater including radiative branch (Ref. 30).
BEAM-FOIL OBSERVATIONS OF Na I DOUBLY-EXCITED STATES

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Received 30 September 1974

We identify a line at 3882.8 Å as the 3s 3p $^4$D$_{7/2}$ – 3s 3d $^4$F$_{9/2}$ transition in Na I. 2p–3s transitions of Na I are observed close to the corresponding Na II resonance lines at 372 Å and 376 Å.

Sodium ground state 1s$^2$2s$^2$2p$^6$ 3s
Excite one 2p electron to n=3 shell and higher… -> quartet states
What are the lowest quartet states? Are they stable?
Fig. 2. A foil-excited spectrum from a 30 keV sodium beam. The doubly-excited Na I transition $3s\, 3p\, {}^4D_{7/2} - 3s\, 3d\, {}^4F_{9/2}$ is indicated at 3882.8 Å.