

Total angular momentum of the electron

$$J = L + S \quad \text{--- (15)}$$

and $J^2 = L^2 + 2L \cdot S + S^2 \quad \text{--- (16)}$

so that

$$L \cdot S = \frac{1}{2} (J^2 - L^2 - S^2) \quad \text{--- (17)}$$

Functions $\psi_{nlm_l m_s}$, given by eqⁿ(12), which are simultaneous eigenfunctions of the operators H_0, L^2, S^2, L_z and S_z are not adequate because $L \cdot S$ does not commute with L_z or S_z .

Satisfactory zero-order wave functions may be obtained by ~~the~~ forming certain linear combinations of the functions $\psi_{nlm_l m_s}$.

Consider new wave functions $\psi_{nlj m_j}$ which are eigenstates of the operators H_0, L^2, S^2, J^2 and J_z and the corresponding eigenvalues being $\hbar^2 n(n+1)$, $\hbar^2 l(l+1)$, $\hbar^2 s(s+1)$, $\hbar^2 j(j+1)$ and $m_j \hbar$. In this particular case we have $s = \frac{1}{2}$. Therefore

$$j = l \pm \frac{1}{2}, \quad l \neq 0 \quad \text{--- (18)}$$

$$j = \frac{1}{2}, \quad l = 0 \quad \text{--- (19)}$$

and $m_j = -j, -j+1, \dots, +j \quad \text{--- (20)}$

We can form the functions $\psi_{nlj m_j}$ from linear combinations of the functions $\psi_{nlm_l m_s}$.

Since $L \cdot S$ commutes with L^2, S^2, J^2 and $J_z \rightarrow$ the new zero-order wavefunctions ψ_{nljm_j} form a satisfactory basis set in which the operator $L \cdot S$ is diagonal (hence the perturbation H_2^1 is diagonal)

Using eqⁿs $H_2^1 = \xi(r) L \cdot S$
 and $L \cdot S = \frac{1}{2} (J^2 - L^2 - S^2)$

We see that for $l \neq 0$, the energy shift due to the term H_2^1 is given by

$$\Delta E_2 = \left\langle \psi_{nljm_j} \left| \frac{1}{2} \xi(r) [J^2 - L^2 - S^2] \right| \psi_{nljm_j} \right\rangle$$

$$= \frac{\hbar^2}{2} \langle \xi(r) \rangle \left[j(j+1) - l(l+1) - \frac{3}{4} \right]$$

(21)

$\langle \xi(r) \rangle \rightarrow$ average value of $\xi(r)$ in the state ψ_{nljm_j}

Fine Structure alkali atoms

All the energy levels of the valence electron in an alkali (except for those with $l=0$) are split into two.

One level $\Rightarrow j = l + \frac{1}{2}$
 and other $j = l - \frac{1}{2}$.

The interaction causing this splitting is the spin-orbit interaction.

The shift in energy due to this effect is given by

$$\Delta E = \frac{1}{2} \lambda_{ne} [j(j+1) - l(l+1) - \frac{3}{4}] \quad \text{---(22)}$$

Constant λ_{ne} is \propto to the expectation value of $r^{-1} dV(r)/dr$, $V(r) \rightarrow$ effective central potential in which the valence electron moves:

$$\lambda_{ne} = \frac{\hbar^2}{2m^2c^2} \left\langle \frac{1}{r} \frac{dV(r)}{dr} \right\rangle = \hbar^2 \langle z(r) \rangle \quad \text{---(23)}$$

Magnitude of λ_{ne} can be estimated by using $V(r)$ as calculated by the Hartree-Fock method.

It is much larger than for atomic hydrogen and other relativistic corrections which are important for hydrogen are negligible.

Spin-orbit splitting of the (n_0l) levels of the alkalis

		ΔE
Li	$n_0 = 2$	0.337 cm ⁻¹ 0.42 eV
Na	$n_0 = 3$	17.2 cm ⁻¹ 21 eV
K	$n_0 = 4$	57.7 cm ⁻¹ 72 eV

For a given atom \rightarrow the splitting decreases with increasing n and l . (35)

For an iso-electronic sequence of positive ions the splitting increases with the charge $\tilde{Z}e$ on the (nucleus + core), behaving like \tilde{Z}^4 for large \tilde{Z} .

Using the Hartree-Fock potential λ_{nl} is found to be positive and the level with $j = 3/2$ has greater energy than with $j = 1/2$.

True for all terms of Li and true for the lower-lying states of the other alkalis.

For $2p$ terms in Al and K and for many other higher terms, the normal order is inverted.

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due to exchange interactions between the valence and core-electrons and other small interactions with the core.

The one-electron selection rules require $\Delta l = \pm 1$ and $\Delta j = 0, \pm 1$.

⇒ The principal and sharp series do lines corresponding to $2P_{3/2, 1/2} \leftrightarrow 2S_{1/2}$

transitions are doublets while the diffuse

series $2D_{5/2, 3/2} \rightarrow 2P_{3/2, 1/2}$ and the

fundamental series $2F_{7/2, 5/2} \rightarrow 2D_{5/2, 3/2}$

are ~~triplets~~ triplets.