PH 585 AMO

Lecture #18

Periodic table

Recall; $H = H_c + H_1$; $H_c \Psi_c = E_c \Psi_c$

H_c ↑ central; H_1: perturb.

$$H_c = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m} \vec{\nabla}^2_{\vec{r}_i} + V(r_i) \right) \qquad E_c = \sum_i E_i$$

$$\Psi_c(q_1, q_2, \ldots q_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P\, u_\alpha(q_1) u_\beta(q_2) \ldots u_\nu(q_N)$$

P ↑ permutation of electron coordinates

$$u_{n l m_l m_s}(q) = R_{nl}(r)\, Y_{l m_l}(\theta, \varphi)\, \chi_{1/2, m_s}$$

$$-\frac{1}{2}\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2}\right] R_{nl}(r) + V(r) R_{nl}(r) = E_{nl} R_{nl}(r)$$

If $V(r) = -\frac{Ze^2}{r(4\pi\epsilon_0)} \Rightarrow E_n \uparrow$ as $n \uparrow$

If $V(r)$ is something else $\Rightarrow E_{nl} \uparrow$ as $n + l \uparrow \Rightarrow$

— 3d — 4p
— 3p — 4s
— 3s
— 2p
— 2s

— 1s

Note: $E_{4s} < E_{3d}$

(4s: 4+0; 3d: 3+2)

Z: nuclear charge (⇑ atomic number)

Ground state of neutral atoms: Z electrons occupy the lowest individual energy levels

Valence electrons: those in the sub-shell of highest energy

↑ less tightly bound

Electron configuration: filling up shells

Z	K-shell (n=1)		Z	L-shell (n=2)		Z	M-shell (n=3)
1	(H)	$1s$	3	(Li)	$1s^2 2s$	11	(Na)
2	(He)	$1s^2$	4	(Be)	$1s^2 2s^2$	18	(Ar)
			5	(B)	$1s^2 2s^2 2p$		
			10	(Ne)	$1s^2 2s^2 2p^6$ ($1s^2$ = (He))		

M-shell (n=3):

11 (Na) $[Ne] 3s$

18 (Ar) $[Ne] 3s^2 3p^6$

Then, since $E_{4s} < E_{3d}$ ⇓

19 (K) $[Ar] 4s$

20 (Ca) $[Ar] 4s^2$

21 (Sc) $[Ar] 4s^2 3d$

⋮

29 (Cu) $[Ar] 4s\, 3d^{10}$

first transition (or iron) group:

24 (Cr) $[Ar] 4s\, 3d^5$

25 (Mn) $[Ar] 4s^2 3d^5$

↑ competition in filling energy levels, since $E_{4s} \sim E_{3d}$

Second transition group (or palladium): $(Z = 39 \text{ to } 48) \Leftrightarrow n = 4$

Third — " — (or platinum): $(Z = 71 \text{ to } 80) \Leftrightarrow n = 5$

} competition between nd and $(n+1)s$

Rare-earth elements (lanthanides): $(Z = 57 - 70) \leftrightarrow 4f$ vs $5d$

Actinides $(Z = 89 - 102) \Leftrightarrow 5f$ vs $6d$

Ionization potential ⇒ non-monotonic in Z
(in contrast to (H)-like ions!)

Maximum at full shells (noble gases – He, Ne, Ar, Kr, Xe, Rn) ← chemically inert

Smallest for alkalis (Li, Na, K, Rb, Cs, Fr) → 1 valence electron

chemically reactive

halogens (F, Cl, Br, I) ← 1 electron missing to fill the shell completely

Note: all of this is due to the Pauli exclusion principle (otherwise all electrons would be in 1s state, and all atoms would be alike)

So, how do we calculate energies? ⇒ need $V(r)$ ⇒

know that at $r \to 0$ $V(r) \to -\frac{Ze^2}{4\pi\epsilon_0 r}$

$r \to \infty$ $V(r) \to -\frac{e^2}{4\pi\epsilon_0 r}$ (neutral atom)

intermediate r $V(r)$ – ?

→ Hartree-Fock; self-consistent field

↓ Thomas-Fermi:

find $V(r)$, $\rho(r)$ ⇐ N-electron atom as a Fermi electron gas confined by $V(r)$

↑ electron density