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Lecture #32

Periodic Table

How do we know the exp. energy of He is -78.975 eV ?

Shine UV on an atom of different light frequencies until an electron comes off.

Find $h\nu = 24.6 \text{ eV}$ for light which emits electrons (ionizes He atom). Note higher frequency light also emits electrons and they have higher E but lower frequency light does not.

Note this is one of the highest thresholds for ionization of any atom. H^+ only takes 13.6 eV to get an electron off of H.

Once you get one electron off you have a He^+ ion. Nucleus has $Z=2$ but only one electron.

You could repeat the exp. with different UV light to find $h\nu$ to kick second e^- off.

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and leave a bare nucleus. Since the system is positively charged expect it to take more energy > 24.6 eV

Note, we know the energy this time. With only one remaining e^- system is an H like ion with $Z=2$

$$E = -Z^2 13.6 \text{ eV} = -54.4 \text{ eV}$$

Thus need $h\nu = 54.4$ eV to get 2nd electron off.

$$E_{\text{tot}} = -24.6 \text{ eV} - 54.4 \text{ eV} = -79.0 \text{ eV}$$

Total E of He atom.

Periodic table

As a crude 1st approx. for atoms heavier than He continue to ignore $e-e$ repulsion.

Independent particle model

Just put electrons into orbitals ψ_{nlm} two at a time 2

two \leftrightarrow spin triplet state $\frac{1}{\sqrt{2}} \uparrow\downarrow - \downarrow\uparrow$

Example Li ($Z=3$)

Configuration: $(1s)^2 2s$

Notation 19th Century spectroscopy

$l=0$	\leftrightarrow	s	state	(sharp)
1	\leftarrow	p	state	(principal)
2	\leftrightarrow		state	(diffuse)
3	\leftrightarrow	f	state	(fine)
4	\leftrightarrow	g	state	
5	\leftarrow	h	state	

Energy in H atom only depends on n
not l .

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) \approx \psi_{100}(r_1) \psi_{100}(r_2) \psi_{200}(r_3) |\text{spin}\rangle$$

$$|\text{spin}\rangle = \frac{1}{\sqrt{2}} (\uparrow\downarrow - \downarrow\uparrow) \quad \uparrow \quad \text{for example}$$

1 2 3 : particle

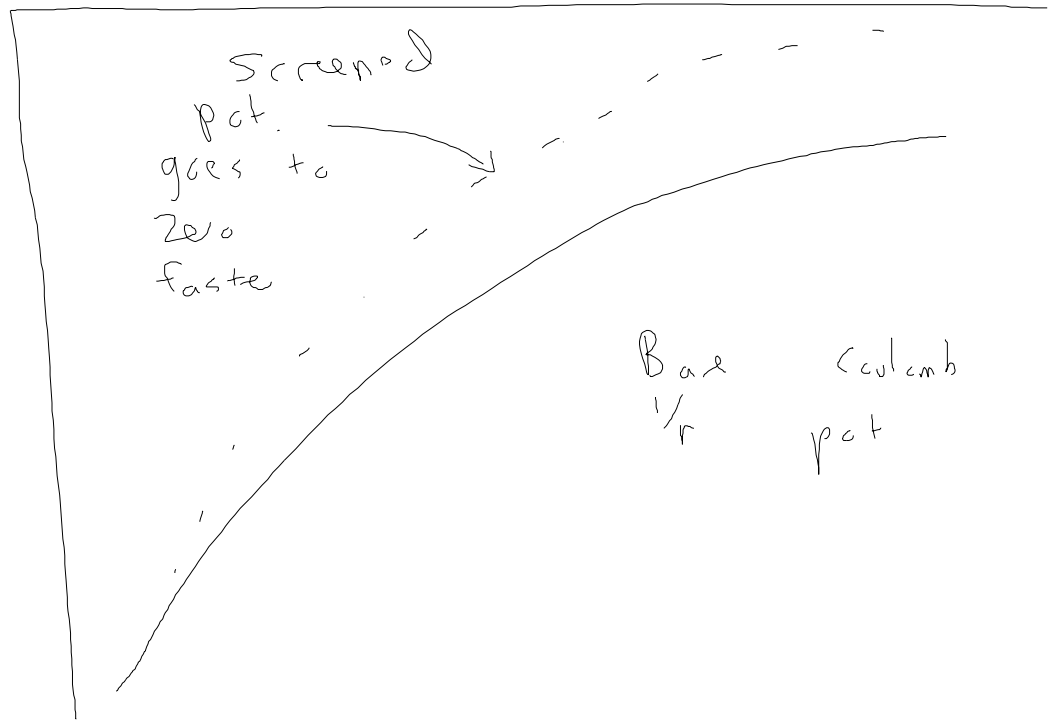
3rd electron in Li sees a screened
Coulomb pot.

$$\rho_{\text{total}}(r) = +Ze\delta(\vec{r}) + \rho_{1s \text{ core}}(r)$$

ρ_{total} charge density \rightarrow $\delta(\vec{r})$ Nucleus $\rho_{1s \text{ core}}$ electron cloud from two 1s electrons

$$\rho_{1s \text{ core}}(r) \approx -2e |\psi_{100}(r)|^2$$

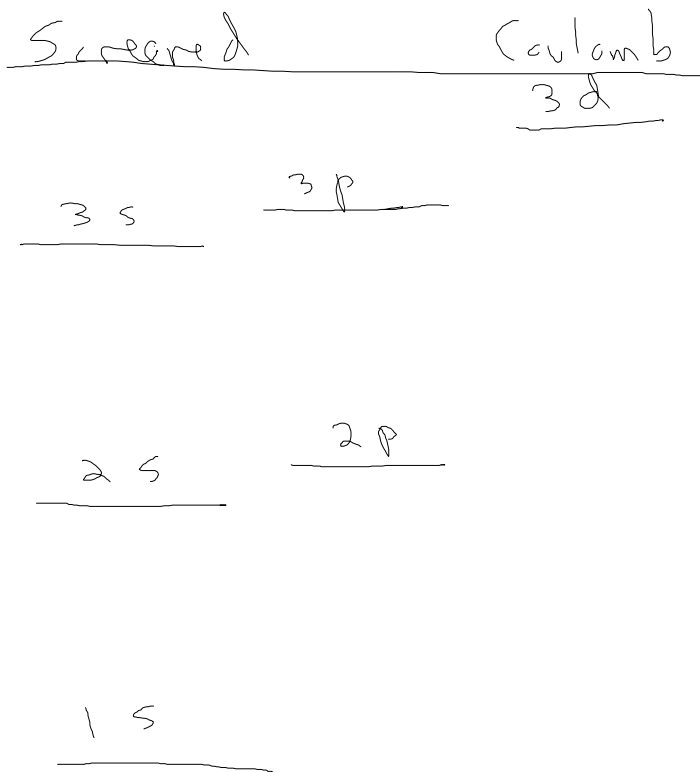
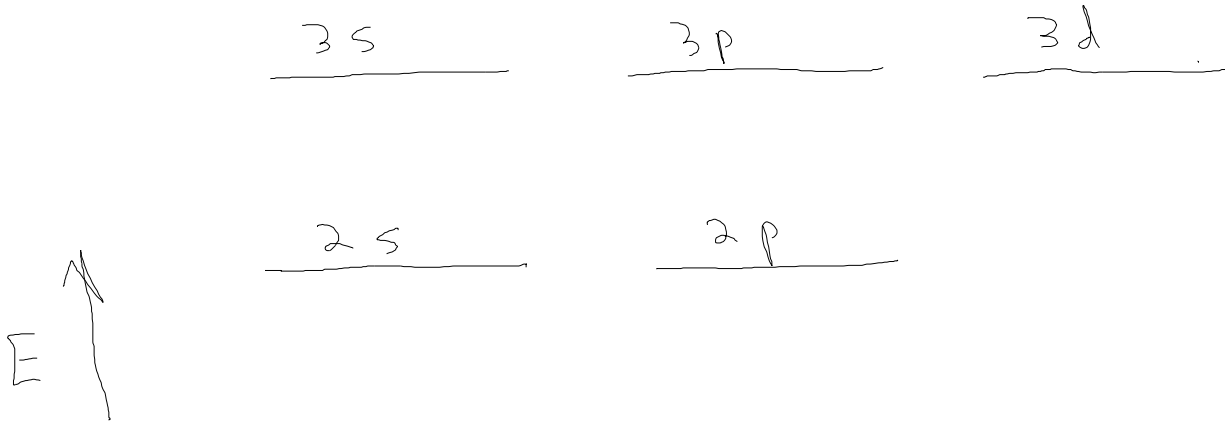
$V(r)$



Solve S. equation in pot. $V(r)$
 Note $V(r)$ found from $\rho_{\text{total}}(r)$
 by solving Maxwell eq.

Since $V(r)$ goes to zero faster
 than $1/r$ it lifts degeneracy
 between different l states

Potential $\propto 1/r$ pert.



low l states are lower in E than high l states. Cent. barrier keeps particles away from small r region where pot is attractive 5

Thus Li is $(1s)^2 2s$
rather than $(1s)^2 2p$

Keep going: Carbon for example $Z=6$

Configuration: $(1s)^2 (2s)^2 (2p)^2$

There are three $2p$ states $m = -1, 0, 1$
thus can put at most 6 electrons
 3×2 spins in $2p$ orbitals

Ne ($Z=10$): $(1s)^2 (2s)^2 (2p)^6$

Shell structure: closed shells have
high ionization thresholds and lead
to almost inert noble gases

Examples He, Ne, Ar

Configuration of Ar: Ne ($Z=10$) $(3s)^2 (3p)^6$
 $Z=18$

In contrast atoms with only one
electron outside of a closed shell
have very low ionization thresholds
and are very reactive Li ($Z=3$),
Na ($Z=11$) configuration $(1s)^2 (2s)^2 (2p)^6 (3s)^1$
K ($Z=19$) configuration (Ar) 4s

Identical Particles Problem 5.3

$$\Psi_{\pm}(\vec{r}_1, \vec{r}_2) = A [\psi_a(\vec{r}_1) \psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1) \psi_a(\vec{r}_2)]$$

What is A ?

Assume ψ_a, ψ_b are normalized and orthogonal.

$$\int d^3r \psi_a^*(r) \psi_a(r) = 1 \quad \int d^3r |\psi_b|^2 = 1$$

assume $a \neq b$

$$\int d^3r \psi_a^* \psi_b = 0$$

$$\int d^3r_1 \int d^3r_2 \psi_{\pm}^* \psi_{\pm} = A^* A$$

$$\int d^3r_1 \int d^3r_2 [\psi_a^*(r_1) \psi_b^*(r_2) \pm \psi_b^*(r_1) \psi_a^*(r_2)]$$

$$[\psi_a(r_1) \psi_b(r_2) \pm \psi_b(r_1) \psi_a(r_2)] = 1$$

$$\therefore A^* A \left[\int d^3r_1 \int d^3r_2 |\psi_a(r_1)|^2 |\psi_b(r_2)|^2 \right.$$

$$\pm \int d^3r_1 \int d^3r_2 \psi_a^*(r_1) \psi_b(r_1) \psi_b^*(r_2) \psi_a(r_2)$$

$$\pm \int d^3r_1 \int d^3r_2 \psi_b^*(r_1) \psi_a(r_1) \psi_a^*(r_2) \psi_b(r_2)$$

$$\left. + \int d^3r_1 \int d^3r_2 |\psi_b(r_1)|^2 |\psi_a(r_2)|^2 \right]$$

$$= A^* A [1 \pm 0 \pm 0 + 1] = 1 \quad 7$$

$$\Rightarrow A = \frac{1}{\sqrt{2}}$$

If $a = b$ then cross terms are identical to diagonal terms

$$A^T A \begin{bmatrix} 1 & \pm 1 & \pm 1 & \pm 1 \end{bmatrix} = 1$$

Only + sign is relevant / - gives ident. = 0

$$A = \frac{1}{2}$$

$$\begin{aligned} \Psi_+(r_1, r_2) &= \frac{1}{2} \left[\Psi_a(r_1) \Psi_a(r_2) + \Psi_a(r_2) \Psi_a(r_1) \right] \\ &= \Psi_a(r_1) \Psi_a(r_2) \end{aligned}$$

Wave func all ready symmetric