Lecture #32  Periodic Table

How do we know the energy of He is $-78.975 \text{ eV}$?

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

Find $h
\nu = 24.6 \text{ eV}$ for light which emits electrons (ionizes the 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. It only takes $13.6 \text{ eV}$ 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.
and leave a bare nucleus. Since the system is positively charged, expect it to take more energy \( > 24.6 \text{ eV} \).

Note: We know the energy of this type. With only one remaining electron, the system is an H-like ion with \( Z = 2 \).

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

Thus, need \( hν = 54.4 \text{ eV} \) to get 2nd electron off.

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

Total \( E \) of the 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 \( \psi_{nlm} \) two at a time.
two $\leftrightarrow$ spin triplet state $\frac{1}{2} \uparrow \downarrow - \uparrow \downarrow$

Example: Li ($Z = 3$)

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

Notation 19th Century spectroscopy

$l = 0 \leftrightarrow s$ state (sharp)

1 \leftrightarrow p$ state (principal)

2 \leftrightarrow d$ state (differential)

3 \leftrightarrow f$ state (fine)

4 \leftrightarrow g$ state

5 \leftrightarrow h$ state

Energy in H atom only depends on $n$ not $l$.

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

$|\text{spin}\rangle = \frac{1}{\sqrt{2}} (|\uparrow \downarrow - \downarrow \uparrow\rangle \uparrow$ for example 1, 2, 3 \text{ particle}

3rd electron in Li sees a screened Coulomb pot.
\[ \rho_{\text{total}}(r) = +3eS(\vec{r}) + \rho_{\text{is core}}(r) \]

Charge density

Nucleus

Electron cloud from two is elections

\[ P_{\text{is core}} = -2e |\psi_{\text{loc}}(r)|^2 \]

\[ V(r) \]

Solve 5.

Equation in pot. \( V(r) \)

Note \( V(r) \) found from \( P_{\text{total}}(r) \)

by solving Maxwell eq.

Since \( V(r) \) goes to zero fast, then \( 1/r \) lifts degeneracy.

Be tween different \( l \) states.
Put it in pot

15

25

35

3d

2d

3d

3d

3d

States: High or lower

Low barriers: states barrier keeps small away from market

1/3 Attention: 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 \(\times\) 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 \((Ar)\) \((4s)^1\)
Identical Particles Problem 5.3

\[ \psi _{+}(\mathbf{r}, \mathbf{r'}) = A \left[ \psi _{a}(\mathbf{r}, \mathbf{r'}) \psi ^{*}_{b}(\mathbf{r}, \mathbf{r'}) \pm \psi _{b}(\mathbf{r}, \mathbf{r'}) \psi ^{*}_{a}(\mathbf{r}, \mathbf{r'}) \right] \]

What is \( A \)?

Assume \( \psi _{a}, \psi _{b} \) are normalized and orthogonal.

\[ \int d^3r \, \psi _{a}(\mathbf{r})^\dagger \psi _{a}(\mathbf{r}) = 1 \quad \int d^3r \, |\psi _{b}(\mathbf{r})|^2 = 1 \]

Assume \( a \neq b \)

\[ \int d^3r \, d^3r' \, \psi _{a}(\mathbf{r})^\dagger \psi _{b}(\mathbf{r}) = 0 \]

\[ \int d^3r \, d^3r' \, \left[ \psi _{a}(\mathbf{r})^\dagger \psi _{b}(\mathbf{r}) + \psi _{b}(\mathbf{r})^\dagger \psi _{a}(\mathbf{r}) \right] = \Delta \]

\[ \int d^3r \, d^3r' \left[ \psi _{a}(\mathbf{r})^\dagger \psi _{b}(\mathbf{r}) \psi _{b}(\mathbf{r})^\dagger \psi _{a}(\mathbf{r}) + \psi _{b}(\mathbf{r})^\dagger \psi _{a}(\mathbf{r}) \psi _{a}(\mathbf{r})^\dagger \psi _{b}(\mathbf{r}) \right] = 1 \]

\[ = A^* A \left[ \int d^3r \, d^3r' \, |\psi _{a}(\mathbf{r})|^2 |\psi _{b}(\mathbf{r})|^2 \right] \]

\[ + \int d^3r \, d^3r' \, \psi _{a}(\mathbf{r})^\dagger \psi _{b}(\mathbf{r}) \psi _{b}(\mathbf{r})^\dagger \psi _{a}(\mathbf{r}) + \psi _{b}(\mathbf{r})^\dagger \psi _{a}(\mathbf{r}) \psi _{a}(\mathbf{r})^\dagger \psi _{b}(\mathbf{r}) \]

\[ + \int d^3r \, d^3r' \left[ \psi _{a}(\mathbf{r})^\dagger \psi _{b}(\mathbf{r}) \psi _{b}(\mathbf{r})^\dagger \psi _{a}(\mathbf{r}) \right] \]

\[ = A^* A \left[ 1 + 0 + 0 + 1 \right] = 1 \]
\[ A = \frac{1}{\sqrt{2}} \]

IF \( a = b \) then cross terms are identical to diagonal terms.

\[ A^2 A \begin{bmatrix} 1 & 1 & 1 & 1 \end{bmatrix} = 1 \]

Only \(+\) sign is relevant \(-\) gives identity. \( = 0 \)

\[ A = \frac{1}{2} \]

\[ \Psi_{+}(r_1, r_2) = \frac{1}{2} \left[ \Psi_{a_1}(r_1) \Psi_{a_2}(r_2) + \Psi_{a_2}(r_1) \Psi_{a_1}(r_2) \right] \]

\[ = \Psi_{a_1}(r_1) \Psi_{a_2}(r_2) \]

Wave func all ready symmetric