Multi-electron atoms

Note Title 09-11-2009

1. The number of radial nodes in a 3s atomic orbital is
(a) 0 (b) 1 (c) 2 (d) 3.

2. An atomic orbital has 2 angular nodes and 1 radial node. It is a (a) 2p (b) 3p (c) 3d (d) 4d orbital.

3. Among the designations
I) n=3, l=2, m=-1 II) n=3, l=1, m=0 III)n=3, l=0, m=-1 IV)n=3, l=2, m=0 V) n=3,l=3,m=-2 which does not describe an allowed state for an electron in an atom?
(a)II and IV (b) I and III (c) III and IV (d) IV and V.

Rigid rotor eigenfunctions - Y_{lm}

Φ angular wavefunctions

$$L^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm}$$

$$L_z Y_{lm} = m\hbar Y_{lm}$$

s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{z^2}, $d_{x^2-y^2}$

$$L_z p_z = L_z Y_{10} = 0\hbar Y_{10}$$

$$L^2 Y_{10} = 1(1+1)\hbar^2 Y_{10}$$

$L_z \; p_x = ?$

$\hookrightarrow$ in the Y_{lm} notation

$Y_{lm} = N_{lm} P_{lm}(\theta) e^{im\varphi}$

$p_x = \dfrac{Y_{11} + Y_{1-1}}{\sqrt{2}} \qquad \dfrac{c e^{i\varphi} + c e^{-i\varphi}}{\sqrt{2}}$

$d_{z^2} \rightarrow$ eigenfunction of L_z

d_{z^2}

$d_{zx} \pm d_{zy}$

$d_{zx} + d_{zy}$

$\langle L_z \rangle = \int p_x^* \left(-i\hbar \dfrac{\partial}{\partial \varphi}\right) p_x \, d\tau$

$= 0$

Helium atom

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\nabla_1^2}_{1} - \underbrace{\frac{\hbar^2}{2m}\nabla_2^2}_{2} - \underbrace{\frac{2e^2}{r_{13}}}_{3} - \underbrace{\frac{2e^2}{r_2}}_{4} + \frac{e^2}{r_{12}}$$

with a nuclear charge $q = +2$:

$1+3$ = (H-atom) like Hamiltonian

$2+4$ = "

$\frac{1}{2}$ =

Zeroth approximation:

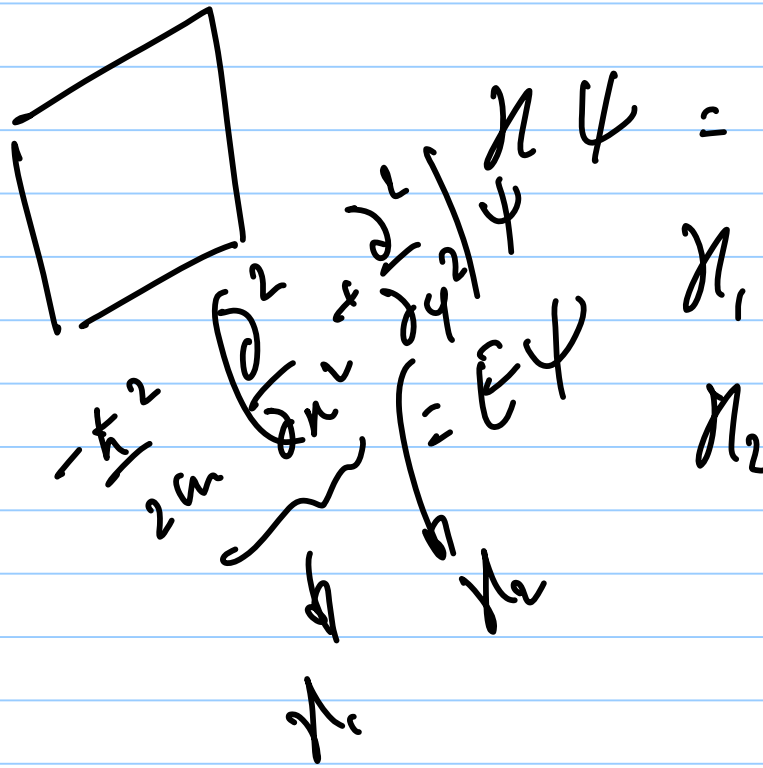
$$\hat{\mathcal{H}} = \mathcal{H}_1 + \mathcal{H}_2$$

$$\mathcal{H}\psi = (\mathcal{H}_1 + \mathcal{H}_2)\psi = E\psi$$

$$\mathcal{H}_1 \psi_1 = \epsilon_1 \psi_1$$

$$\mathcal{H}_2 \psi_2 = \epsilon_2 \psi_2$$

$$\psi = \psi_1 \psi_2, \quad E = \epsilon_1 + \epsilon_2$$



$$\Psi = \Psi_{1s}(1)\,\Psi_{1s}(2)$$

$$\Psi_{1s} = e^{-Zr/a_0} \quad \rightarrow \quad Z = 2$$

$$\epsilon_1 = Z^2 \times H_s$$

$$E = 2 \times \underbrace{\left(Z^2 \times H_s\right)}_{13.6\,eV} = -108.8\,eV$$

empirical $-75\,eV$ [He $\rightarrow$ $He^{+2} + 2e$

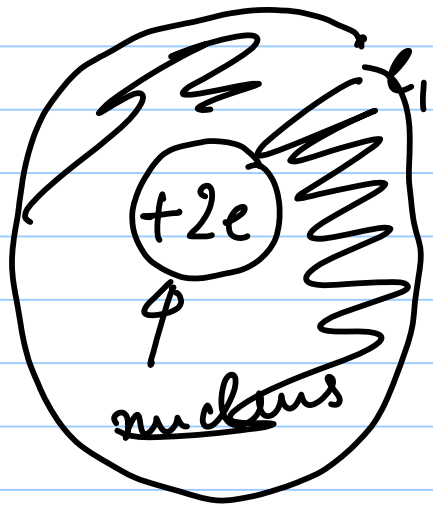
$He \rightarrow He^{+} + e$

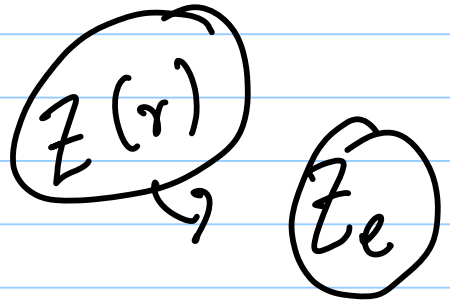
$-54.4\,eV$ $He^{+} \rightarrow He^{2+} + e \rightarrow$ IP!

First approximation

$$\psi = \underbrace{\psi_{1s}(1)\,\psi_{1s}(2)}$$

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = \int \psi_{1s}(1)\,\psi_{1s}(2)\,\frac{e^2}{r_{12}}\,\psi_{1s}(1)\,\psi_{1s}(2)\,d\tau_1\,d\tau_2$$





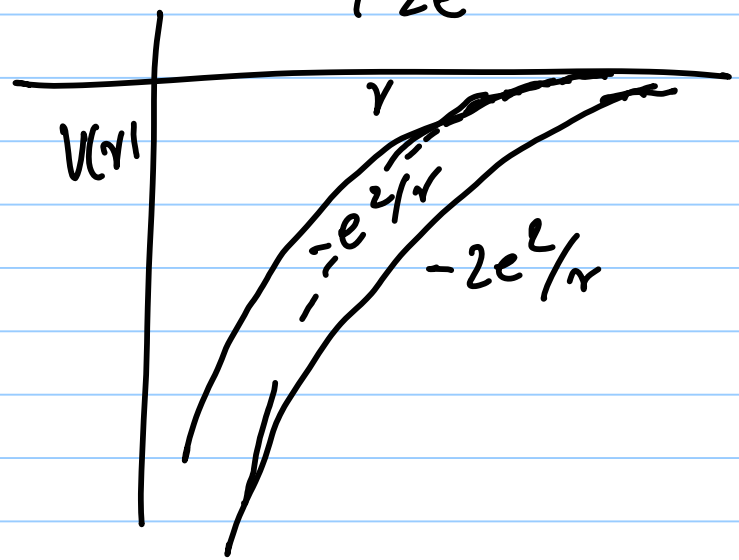
e_2

$r_2 > r_1$

$+1e$

$r_2 < r_1$

$+2e$



$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}$$ significant

T = constant

Tman

$e^{-x} + x = 5$

$e^{-x} = 0$

1st pass e

$x_0 = 5$

2nd pass

$e^{-5} + x = 5$

$x_1 = 4.98$

$-4.98 \; dx = x_2$

$\psi^{(0)} = \psi_{1s}(1)\,\psi_{1s}(2)$

Zeroth order approximation

$$\left\langle \frac{e^2}{r_{12}} \right\rangle = e^2 \int \psi^{(0)} \frac{1}{r_{12}} \psi^{(0)} \, d\tau_1 \, d\tau_2$$

$$\frac{1}{|r_1 - r_2|}$$

proplan of $\epsilon_1 + \epsilon_2$

perturbation

$= 29\ eV$

$-108.8\ eV + 29\ eV: \quad -79\ eV$

$-75\ eV$ (expt'l)

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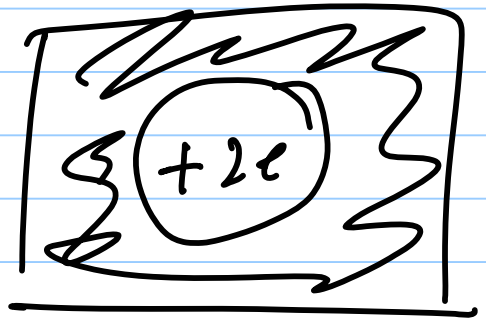
screened nuclear charge



$< Ze$

$\psi: \psi_1 + \psi_2 + \psi_3 - \cdots + \psi_n$

independent e^-

$\Psi = \psi_1 \psi_2 \psi_3 \cdots$

Recap 0) Ignore interelectronic repulsion

$$\Psi_{GS}^{ok} = \psi_{1S}(1)\,\psi_{1S}(2)$$

1) Interelectronic repulsion (perturbation)

Expectation value of

$$\left\langle \frac{1}{r_{12}} \right\rangle = \langle \Psi_{GS} | \frac{1}{r_{12}} | \Psi_{GS} \rangle = \int \Psi_{GS} \frac{1}{r_{12}} \Psi_{GS}\, d\tau_1 d\tau_2$$

; after 4/5 pages of algebra

$$\psi_{1s} = e^{-2r/a_0}$$

$$\psi_{1s}^{(1)} = e^{-Z_e r/a_0}$$ → unknown

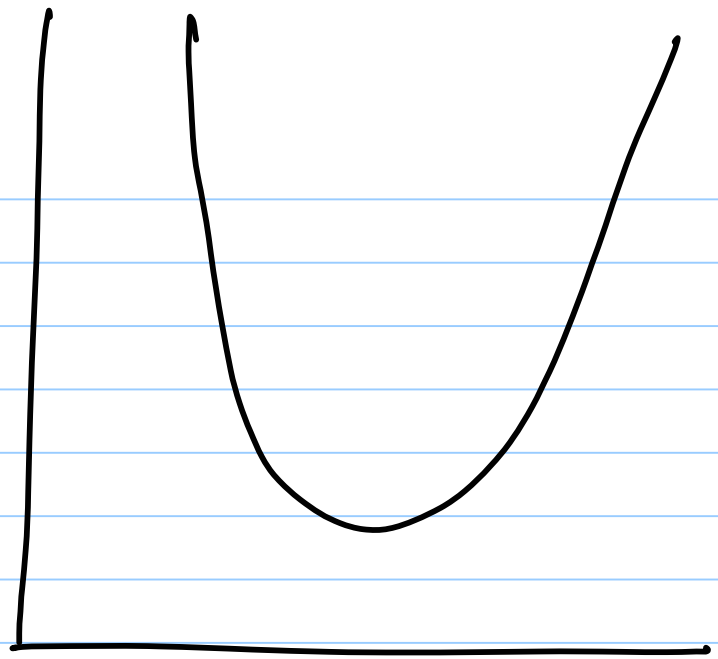
↺ order of approximation

$$\langle \mathcal{H} \rangle = \int \psi_{1s}^{(1)}(1)\, \psi_{1s}^{(1)}(2)\, \hat{\mathcal{H}}\, \psi_{1s}^{(1)}(1)\, \psi_{1s}^{(1)}(2)$$

↺ electron index

$$\hat{\mathcal{H}} = \frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{r_2} + \frac{1}{r_{12}}$$

$$\langle \mathcal{H} \rangle = f(Z_e)$$



$$\frac{\partial [x]}{\partial x_\nu} = 0$$

$$\psi = e^{-Z_e r_1/a_0} \; e^{-(Z_e) r_2/a_0}$$

e^{-Zr/a_0} → intuitive guess

$e^{-ar + br^2 + cr^3 + \cdots}$

$\Sigma[f]$ ← functional

$\frac{\partial T}{\partial a}(a, b, c, \cdots) = 0 \qquad \frac{\partial T}{\partial b} = 0 \cdots$

"Variational principle"

Excited state of Helium

Ground state of Helium $\psi_{1s}(1)\ \psi_{1s}(2)$

$\psi_{1s}(1)\ \psi_{n\ell}(2)$

energies are identical ← electron labels → exchange degeneracy

$\psi_{1s}(2)\ \psi_{n\ell}(1)$

Permutation symmetry

$$P_{12}\ \psi_{1s}(1)\ \psi_{n\ell}(2) = \psi_{1s}(2)\ \psi_{n\ell}(1)$$

$$P_{12}^2\ \psi_{1s}(1)\ \psi_{n\ell}(2) = \psi_{1s}(1)\ \psi_{n\ell}(2)$$

ψ_S

symmetric linear combination → $\psi_{1s}(1)\,\psi_{2s}(2) + \psi_{1s}(2)\,\psi_{2s}(1)$

antisymmetric linear combination → $\psi_{1s}(1)\,\psi_{2s}(2) - \psi_{1s}(2)\,\psi_{2s}(1)$ $\Big\}$ ψ_a

$$P_{12}\,\psi_S = \psi_S$$

$$P_{12}\,\psi_a = -\psi_a$$