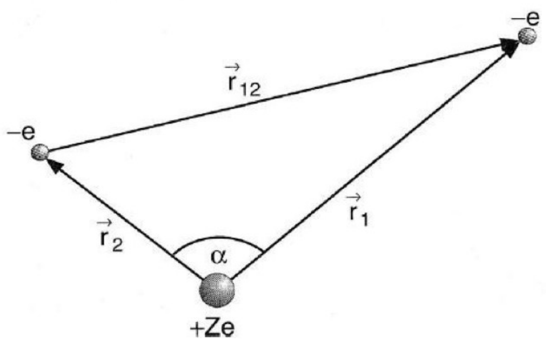
Lecture Wednesday 29 August 2007 (updated 30.08.2007 version)

Topics: Helium atom part 1 - Intro and mainly so called symmetry

Classical schematics of He-like atom – nucleus +Ze + 2 e^-

other 2-electron atoms H^- He Li^+ Be^{++} B^{+++} C^{4+}

1- electron sequence H He^+ Li^{++} Be^{+++} B^{4+} C^{5+} ...... U^{91+}



$$T_1(\mathbf{r}_1) \longrightarrow -\frac{\hbar^2}{2m_e}\nabla_{r_1}^2 \qquad T_2(\mathbf{r}_1) \longrightarrow -\frac{\hbar^2}{2m_e}\nabla_{r_2}^2$$

$$V_1(\mathbf{r}_1) = -\frac{Z\,e^2}{|\mathbf{r}_1|} \longrightarrow -\frac{Z\,e^2}{r_1} \qquad V_2(\mathbf{r}_2) = -\frac{Z\,e^2}{r_2}$$

$$V_{12}(\mathbf{r}_2,\mathbf{r}_2) = +\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|} \longrightarrow +\frac{e^2}{r_{12}}$$

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)$$

$$[T_1(\mathbf{r}_1) + V_1(\mathbf{r}_1) + T_2(\mathbf{r}_2) + V_2(\mathbf{r}_2) + V_{12}(\mathbf{r}_2,\mathbf{r}_2)]\,\Psi(\mathbf{r}_1,\mathbf{r}_2) = E\,\Psi(\mathbf{r}_1,\mathbf{r}_2)$$

$$\left[-\frac{\hbar^2}{2m_e}\nabla_{r_1}^2 - \frac{Z\,e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_{r_2}^2 - \frac{Z\,e^2}{r_2} + \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}\right]\Psi(\mathbf{r}_1,\mathbf{r}_2) = E\,\Psi(\mathbf{r}_1,\mathbf{r}_2)$$

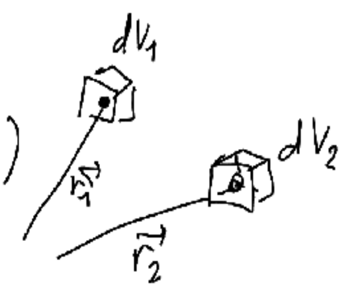
Independent electrons wavefunction: it reflects the probability of independent events, which is a product of probabilities. (the coins throwing etc – independent results). When events are dependent – conditional probabolities – not product

Independent electrons – reflected in $\Psi(\vec{r}_1, \vec{r}_2)$

$P(\vec{r}_1, \vec{r}_2)$ probability density $= |\Psi(\vec{r}_1, \vec{r}_2)|^2$

$dV_1 \; dV_2$

$P(r_1, r_2) = P(\vec{r}_1) \cdot P(\vec{r}_2)$



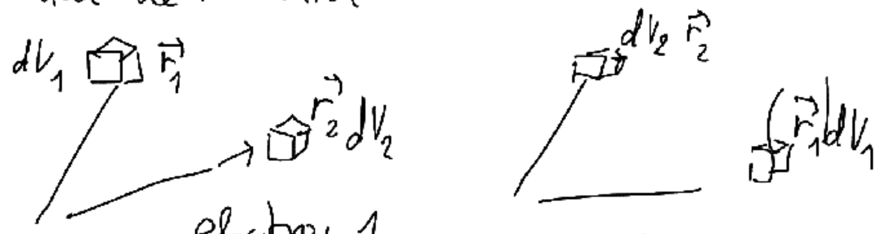
Indep. particles

$$\boxed{\Psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1) \cdot \psi_b(\vec{r}_2)}$$

We will now look at the origin of «Symmetry» Historically – Pauli Principle – and the «Aufbau Principle»

Pauli principle : Aufbau princ. (Buil-up ....)
available states → to every state
1 electron (SPIN)

The "identical" particles
are "indistinguishable"
which one is which



electron 1 . . . r_1 ? ?
" 2 . . . r_2

r_1 ; r_2 and any electron in either $\vec{r}_1$ or $\vec{r}_2$

$$P(\vec{r}_1, \vec{r}_2) = P(\vec{r}_2, \vec{r}_1)$$

1 place – electron 1
2 place – " – 2

Whether dependent or not, the exchange, or replacement (Norwegian: ombytting German Vertauschung ... French ... la symétrie d'échange....) should not change the probability distributions whn the electrons are «just the same» - i.e. impossible to distinguish between them – or identical ... it has a «touch of observation».....

$$\Psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\, \psi_b(\vec{r}_2)$$

not satisfied
$P(r_1 r_2) \neq P(r_2, r_1)$

SO CALLED SYMMETRY

(the only possible explanation)

$$P(r_1, r_2) = P(r_2, r_1)$$

$$|\Psi(r_1, r_2)|^2 = |\Psi(r_2, r_1)|^2$$

Only 2 possibilities

$$\psi(r_1, r_2) = \pm \psi(r_2, r_1)$$

Why not $e^{i\alpha}$ with arbitrary real α

$$\psi(r_1, r_2) = e^{i\alpha}\, \psi(r_2, r_1) = \left(e^{i\alpha}\right)^2 \psi(r_1, r_2)$$

$\boxed{\text{[Exchange operator]}}$

$$\left(e^{i\alpha}\right)^2 = 1$$

→ $2\alpha = 0$ +
→ $2\alpha = 2\pi$ –

Simple «ombytting» or exchange of coordinates can be replaced by mathematical operator – mathematical formalism – EXCHANGE OPERATOR

EXCHANGE OP. A

$$A\,\psi(r_1,r_2) \rightarrow \psi(r_2,r_1)$$

$$A^2\psi = \psi \quad \text{(obviously)} \qquad A\psi = e^{i\alpha}\psi$$

2-electron W.F. can only be → Eigenfunction of A with Eigenvalue $e^{i\alpha}$

$$A\psi = e^{i\alpha}\psi$$

$$AA\psi = e^{i\alpha}e^{i\alpha}\psi$$

$$e^{2i\alpha} = 1$$

Claim

$$A^2 \rightarrow 1$$

because it's obvious

$$\alpha = 0, \pi$$

Funny that it can not be any phase – we can understand the mathematical formulation of saying that the wavefunctions must be eigenstates of exchange,
the $e^{i\alpha}$ is an eigenvalue ...

$$\psi(r_1 r_2) = \psi_a(r_1)\,\psi_b(r_2)$$

$$e^{i\alpha} = 1 \qquad \psi_a(r_1)\,\psi_b(r_2) + \psi_b(r_1)\,\psi_a(r_2)$$

$$e^{i\alpha} = -1 \qquad \psi_a(r_1)\,\psi_b(r_2) - \psi_b(r_1)\,\psi_a(r_2)$$

If $\psi_a(r)$ and $\psi_b(r)$ are normalized (orthogonal)

$$\Psi_S(r_1,r_2) = \frac{1}{\sqrt{2}}\left(\psi_a(r_1)\,\psi_b(r_2) + \psi_b(r_1)\,\psi_a(r_2)\right)$$

$$\Psi_A(r_1,r_2) = \frac{1}{\sqrt{2}}\left(\psi_a(r_1)\,\psi_b(r_2) - \psi_b(r_1)\,\psi_a(r_2)\right)$$

antisymmetric A

Symmetric S

History of spin – Pauli – but «invented» before Pauli – Zeeman effect etc

Spin - additional "wavefunction" part

Pauli invented Spinors ......

two "possible" states

described by some abstract coordinates

$$\begin{bmatrix} \varphi_1(x_1) \\ \varphi_2(x_2) \end{bmatrix}$$ - space dependent spinor

- decomposition over the two possible states

Completely arbitrary, they're called ↑ ↓

CONSTANT SPINOR $\begin{bmatrix} \varphi_1(x_1) \\ \varphi_2(x_2) \end{bmatrix}$ ← up ← down

If independent spin and space

$\Psi_a = \Phi_a \begin{bmatrix} a \\ b \end{bmatrix}$

Homework: show that they are the same functions

$\begin{bmatrix} a \\ b \end{bmatrix}$ a,b constants $\longrightarrow \chi[\sigma_1]$

$$\Psi_a(r_1) \to \Phi_a(r_1)\,\chi_a[\sigma_1]$$

$$\Psi_a(r_1)\,\Psi_b(r_2)$$

$$[\Phi_a(r_1)\chi_a(1)\,\Phi_b(r_2)\chi_b(2)$$

$$-\Phi_b(r_1)\chi_b(1)\,\Phi_a(r_2)\chi_a(2)]$$

[Show that it is the same function]

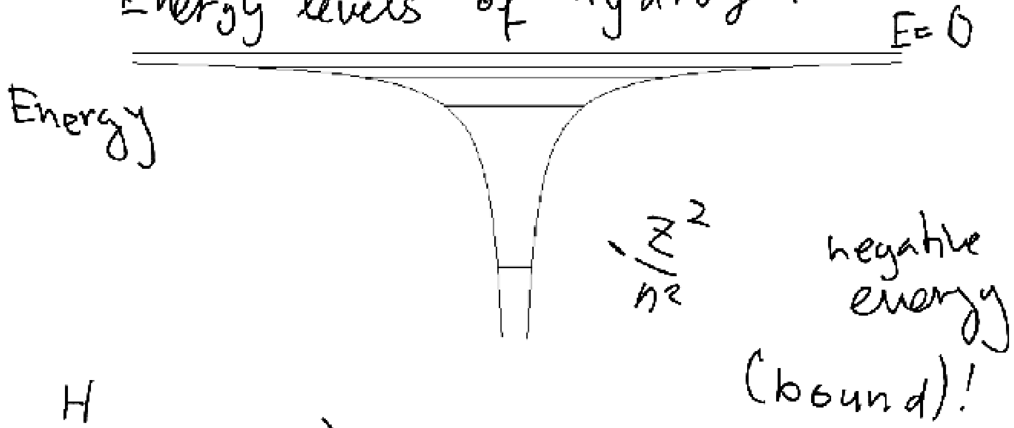
$$[\Phi_a(r_1)\Phi_b(r_2) \pm \Phi_b(r_1)\Phi_a(r_2)][\chi_a(1)\chi_b(2) \mp \chi_b(1)\chi_a(2)]$$

$$\Psi_A(r_1,\sigma_1, r_2\sigma_2) < \begin{matrix} \Phi_S(r_1 r_2)\ \Xi_A(1,2) \\ \Phi_A(r_1 r_2)\ \Xi_S(1,2) \end{matrix}$$

About Ions and hydrogen-like atoms.... beginning of lecture
This belongs to the Hydrogen Atom Reviews

Hydrogen-like or 1-electron

Energy levels of hydrogen-like



H
He^+ (ion) $Z=2$, $q=+1$
Li^{++} -//- $Z=3$ $q=+2$ U^{91+}
Be^{+++} ....

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