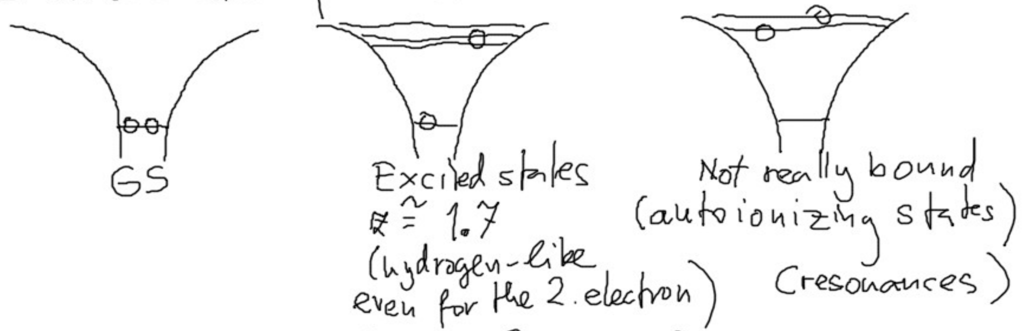
Lecture Wednesday 12. September 2007

Topics Excited states of Helium; Autoionizing states

Excited states of Helium Comment ... the triplets have antisym space functions

Excited states of Helium



$$H = T_1 + T_2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$$

$$\psi_{exc} \approx \left[\varphi_{1s}(r_1)\,\varphi_{n\ell}(r_2)\right]_{\substack{SYM \\ ASYM}}$$

First – look at triplets

$$\psi_{1s,n\ell}(\vec{r}_1\vec{r}_2) \approx \frac{1}{\sqrt{2}}\left(\varphi_{1s}(\vec{r}_1)\,\varphi_{n\ell}(2) - \varphi_{n\ell}(1)\,\varphi_{1s}(2)\right)$$

First evaluate the normalization (zero terms!)

First – look at triplets

$$\psi_{1s,n\ell}(\vec{r}_1\vec{r}_2) \approx \frac{1}{\sqrt{2}}\left(\varphi_{1s}(\vec{r}_1)\,\varphi_{n\ell}(2) - \varphi_{n\ell}(1)\,\varphi_{1s}(2)\right)$$

Normalization:

$$\iint d1\,d2\,|\psi_{1s,n\ell}(1,2)|^2 = \iint \frac{1}{2}\Big\{|\varphi_{1s}(1)|^2|\varphi_{n\ell}(2)|^2 + |\varphi_{n\ell}(1)|^2|\varphi_{1s}(2)|^2 - \underbrace{\varphi_{1s}^*(1)\varphi_{n\ell}(1)}_{\int d1 \to 0}\,\underbrace{\varphi_{n\ell}^*(2)\varphi_{1s}(2)}_{0}$$

$$- \varphi_{n\ell}^*(1)\,\varphi_{1s}(1)\,\underbrace{\varphi_{1s}^*(2)\,\varphi_{n\ell}(2)}_{0} \to \frac{1}{2}(1+1) \to 1$$

We evaluate the normalization, because it is very similar to the evaluation of E_a and E_b below

Evaluation of the whole energy – and then the repulsion integral

$$H = T_1 + T_2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$$

$$\psi_{exc} \approx \left[\varphi_{1s}(r_1)\,\varphi_{nl}(r_2)\right]_{\substack{SYM\\ ASYM}}$$

First – look at triplets

$$\psi_{1s,nl}(\vec{r}_1\vec{r}_2) \approx \frac{1}{\sqrt{2}}\left\{\varphi_{1s}(\vec{r}_1)\,\varphi_{nl}(2) - \varphi_{nl}(1)\,\varphi_{1s}(2)\right\}$$

$$\iint d1\,d2\,\psi^*_{ab}(1,2)\,H\,\psi_{ab}(1,2) \qquad (20\text{ terms})$$

just like the normalization $\qquad (T_1 + V_1)\varphi_a(1) = E_a\varphi_a(1)$

$$E_a + E_b + \int d1\,d2\,\psi^*_{ab}(r_1 r_2)\,\frac{e^2}{r_{12}}\,\psi_{ab}(1,2)$$

20 terms will become 3 terms, but the last splits again to 2 terms

$$\psi^*_{1s,nl}(\vec{r}_1\vec{r}_2) \approx \frac{1}{\sqrt{2}}\left\{\varphi^*_{1s}(\vec{r}_1)\,\varphi^*_{nl}(2) - \varphi^*_{nl}(1)\,\varphi^*_{1s}(2)\right\}$$

$$\varphi_{1s}(1)\,\varphi_{nl}(2) - \varphi_{nl}(1)\,\varphi_{1s}(2)$$

$$\int d1\,d2\,\psi^*_{ab}(r_1 r_2)\,\frac{e^2}{r_{12}}\,\psi_{ab}(1,2)$$

$$\frac{e^2}{2}\Big\{\int d1\int d2\,\varphi_a^*(1)\,\varphi_b^*(2)\,\frac{1}{r_{12}}\,\varphi_a(1)\,\varphi_b(1) \qquad I$$

$$\int d1\int d2\,\varphi_b^*(1)\,\varphi_a^*(2)\,\frac{1}{r_{12}}\,\varphi_b(1)\,\varphi_a(2) \qquad K$$

$$-\int d1\int d2\,\varphi_a(1)^*\,\varphi_b^*(2)\,\frac{1}{r_{12}}\,\varphi_b(1)\,\varphi_a(2) \qquad \begin{matrix}1\to x\\ 2\to y\end{matrix}$$

$$-\int d1\,d2\,\varphi_b^*(1)\,\varphi_a^*(2)\,\frac{1}{r_{12}}\,\varphi_a(1)\,\varphi_b(2) \qquad \begin{matrix}1\to y\\ 2\to x\end{matrix}$$

$$\left.\begin{matrix} -\int d^3x\int d^3y\,\varphi_a^*(x)\,\varphi_b(x)\,\varphi_b^*(y)\,\varphi_a(y)\,\frac{1}{r_{12}} \\ -\int d^3x\int d^3y\,\varphi_a^*(x)\,\varphi_b(x)\,\varphi_b^*(y)\,\varphi_a(y)\,\frac{1}{r_{22}} \end{matrix}\right\} \to I - K$$

2 direct I-terms and 2 exchange terms. We have shown that each pair of the terms are in fact identical – the transformations 1 -> x , 2 -> y and *vice versa*

Repeated from the last slide – and the conclusion

$$\frac{1}{2}\Big\{\int d1\int d2\, \varphi_a^*(1)\,\varphi_b^*(2)\,\frac{1}{r_{12}}\,\varphi_a(1)\,\varphi_b(1)$$

$$\int d1\int d2\, \varphi_b^*(1)\,\varphi_a^*(2)\,\frac{1}{r_{12}}\,\varphi_b(1)\,\varphi_a(2)$$

$$-\int d1\int d2\, \varphi_a(1)^*\,\varphi_b^*(2)\,\frac{1}{r_{12}}\,\varphi_b(1)\,\varphi_a(2) \qquad \begin{matrix}1\to x\\ 2\to y\end{matrix}$$

$$-\int d1\, d2\, \varphi_b^*(1)\,\varphi_a^*(2)\,\frac{1}{r_{12}}\,\varphi_a(1)\,\varphi_b(2)\Big\} \qquad \begin{matrix}1\to y\\ 2\to x\end{matrix}$$

$$= \Big[\int d1\int d2\, \varphi_a^*(1)\,\varphi_b^*(2)\,\frac{1}{r_{12}}\,\varphi_a(1)\,\varphi_b(1)$$

1/2 cancelled

$$-\int d1\int d2\, \varphi_a(1)^*\,\varphi_b^*(2)\,\frac{1}{r_{12}}\,\varphi_b(1)\,\varphi_a(2)\Big]$$

$$= \mathcal{J}_{ab,ab} - \mathcal{K}_{ab,ba}$$

DIRECT TERM EXCHANGE

THE TRIPLET-SINGLET problem can be also explained using this mathematics

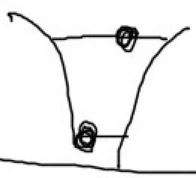
For triplets $E = E_a + E_b + I_{ab} - K_{ab}$

For singlets $E = E_a + E_b + I_{ab} + K_{ab}$ Thus singlets higher energy

Excited states of 1-electron → described with Exchange terms

(look also for: configuration mixing (later)

$$C_1\,\varphi_{1s}(1)\,\varphi_{2s}(2) + C_2\,\varphi_{1s}(1)\,\varphi_{3s}(2) + \dots C_3\,\varphi_{2s}(1)\,\varphi_{2s}(2)$$

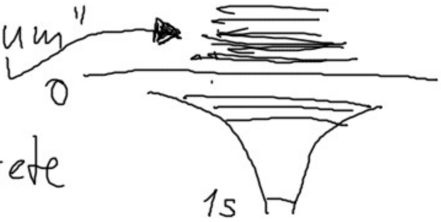


must be refined

The simple picture of 1 configuration» must be refined. This will be discussed for many-electron atoms

Excited states in continuum => have the same energy as free electrons

Excited states "in continuum"



discrete

repulsion is so large that total energy becomes positive

$\varphi_{2s}(1)\,\varphi_{5s}(2)$ → 2 H-like states

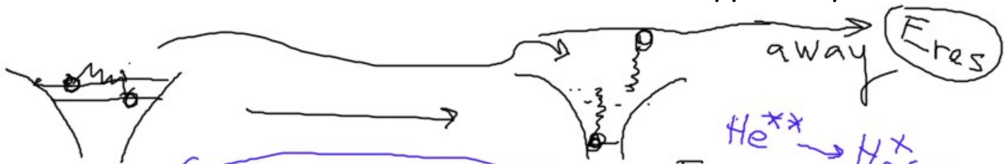
→ but energy > 0

Degenerate energies (eigenvalues) } they mix

One electron can escape

$$E_{2s} + E_{5s} + \left\langle \frac{e^2}{r_{12}} \right\rangle = E_{1s} + E_{continuum}$$

Autoionization and Dielectronic recombination are opposite processes



$He^{**} \to He^+(1s) + e_{res}$

E_1 (autoionization) E_2

* means excitation $E_1 = E_2$

Autoionizing states

Auger effect [Autoionizing of already ionized]

Electron scattering → resonant with E_{res}

← electron

He ion

$\boxed{He^+(1s) + e_{res} \to He^{**}}$

Dielectronic recombination

Dielectronic recombination is «Resonant scattering on ionized helium»

We have discussed Autoionizing states
Dielectronic recombination
Three body recombination
Competition between them

Resonant scattering (time delay) very similar in principle to α - decay

Next topic is Selfconsistent field methods – physics of many electron atoms

Short preview:

Hartree | Hartree – Fock methods

Beyond variational method (analytical mostly)

"Completely" numerical
The differential equations are solved numerically

$$T_1 + V_1 + \underbrace{\int \frac{e^2}{r_{12}} \psi_b^*(2)\,\psi_b(2)\, d^3 r_2}_{\text{known}} \qquad \int \frac{e^2 \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3 r_2 \ \text{known}$$

$$\left\{ T_1 - \frac{Ze^2}{r_1} + W(r_1) \right\} \underbrace{\varphi_a(r_1)}_{\text{unknown} \to \text{solve}} = E_a\, \varphi_a(r_1)$$