IV. 3 Helium-Atom; Singulett und Triplett-System

He $1s^2$ einfachstes Beispiel für Mehrelektronen-Atom

Grundzustand	$1s^2$	$1\,^1S_0$	
angeregte Zustände	$1s\,2s$	$2\,^1S_0$	$2\,^3S_1$
Einelektronen-anregung $1s\,nl$	$1s\,2p$	$2\,^1P_1$	$2\,^3P_{2,1,0}$
	$1s\,3s$	$3\,^1S_0$	$3\,^3S_1$
	$1s\,3p$	$3\,^1P_1$	$3\,^3P_{2,1,0}$
	$1s\,3d$	$3\,^1D_2$	$3\,^3D_{3,2,1}$
		Singulett-System	Triplett-System
historisch		Parahelium	Orthohelium

z.B. keine optischen Übergänge zwischen beiden!

Wichtiges Detail:

1. angeregter Zustand: $2\,^1S_0$ — $1s\,2s$ ····· $2\,^3S_1$ — $1s\,2s$ ↕ ΔE

$\Delta E = 0{,}8\ eV$

2. angeregter Zustand: $2\,^1P_1$ — $1s\,2p$ ····· $2\,^3P_{2,1,0}$ — $1s\,2p$ ↕ ΔE

$\Delta E_{str.} = 0{,}25\ eV$

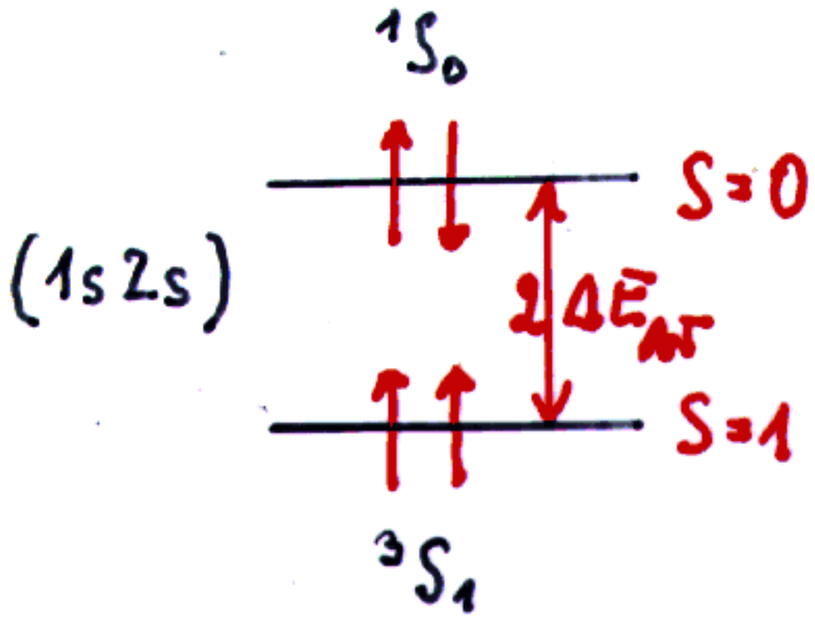
↑↓ ↑↑

ΔE: Austauschaufspaltung

Interatomarer Austausch immer ferromagnetisch!

Parallel-Stellung energetisch günstiger (Hund; fm)

IV. 3 a) Austausch-Integral, -Aufspaltung

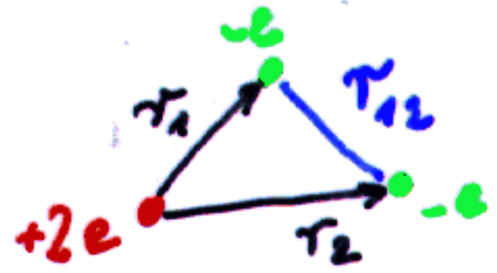


(1s 2s)

(siehe auch VI.1)

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{Coul(e\text{-}e)} = \mathcal{H}_0 + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$E = E_{n_1,n_2} + \Delta E$$



$$\Psi_{S=0}(1,2) = \frac{1}{\sqrt{2}} \left\{ \psi_{1s}(r_1)\,\psi_{2s}(r_2) + \psi_{1s}(r_2)\,\psi_{2s}(r_1) \right\} \cdot \chi^{Spin}_{sing.}$$

$$\Psi_{S=1}(1,2) = \frac{1}{\sqrt{2}} \left\{ \psi_{1s}(r_1)\,\psi_{2s}(r_2) - \psi_{1s}(r_2)\,\psi_{2s}(r_1) \right\} \cdot \chi^{Spin}_{Trip.}$$

$$\Delta E_{S=0} = \Delta E_{Coulomb} + \Delta E_{Austausch}$$

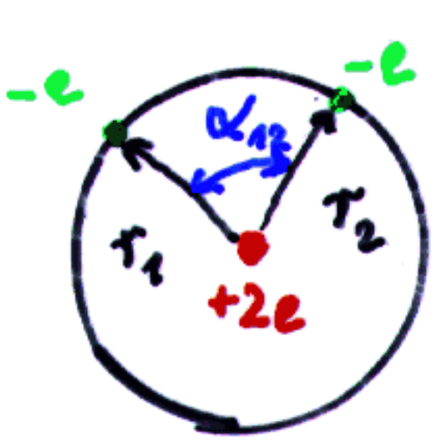
$$\Delta E_{S=1} = \Delta E_{Coulomb} - \Delta E_{Austausch}$$

$$\Delta E = \iint_{1\,2} \Psi^* \frac{e^2}{4\pi\varepsilon_0 r_{12}} \Psi \, d\tau_1 \, d\tau_2$$

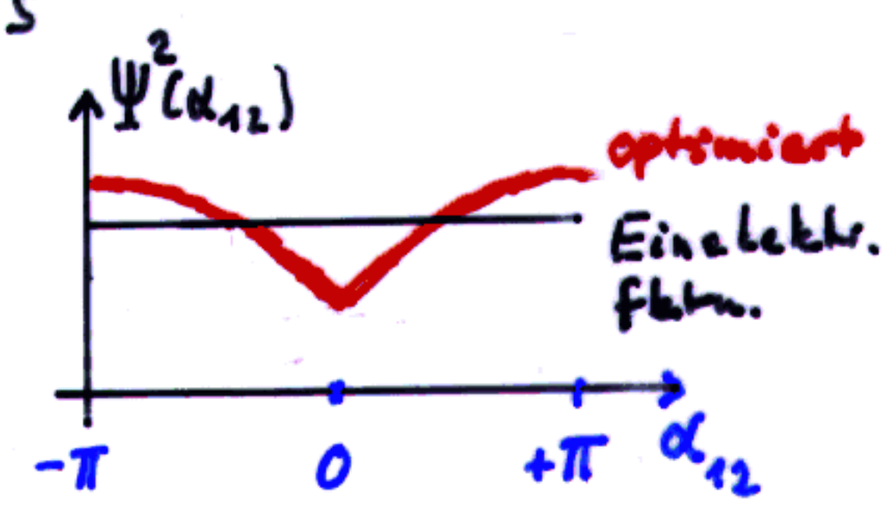
$$\Delta E_{Coul.} = \frac{1}{2} \iint_{1\,2} d\tau_1 \, d\tau_2 \, \frac{e^2}{4\pi\varepsilon_0 r_{12}} \left\{ \psi_{1s}^2(r_1)\,\psi_{2s}^2(r_2) + \psi_{1s}^2(r_2)\,\psi_{2s}^2(r_1) \right\}$$

$$\Delta E_{Aust} = \frac{1}{2} \int_1 \int_2 d\tau_1 \, d\tau_2 \left\{ \psi_{1s}(r_1)\,\psi_{2s}(r_2) \frac{e^2}{4\pi\varepsilon_0 r_{12}} \psi_{1s}(r_2)\,\psi_{2s}(r_1) + \psi_{1s}(r_2)\,\psi_{2s}(r_1) \frac{e^2}{4\pi\varepsilon_0 r_{12}} \psi_{1s}(r_1)\,\psi_{2s}(r_2) \right\}$$

b) Korrelationseffekte im Grundzustand



$1s^2$

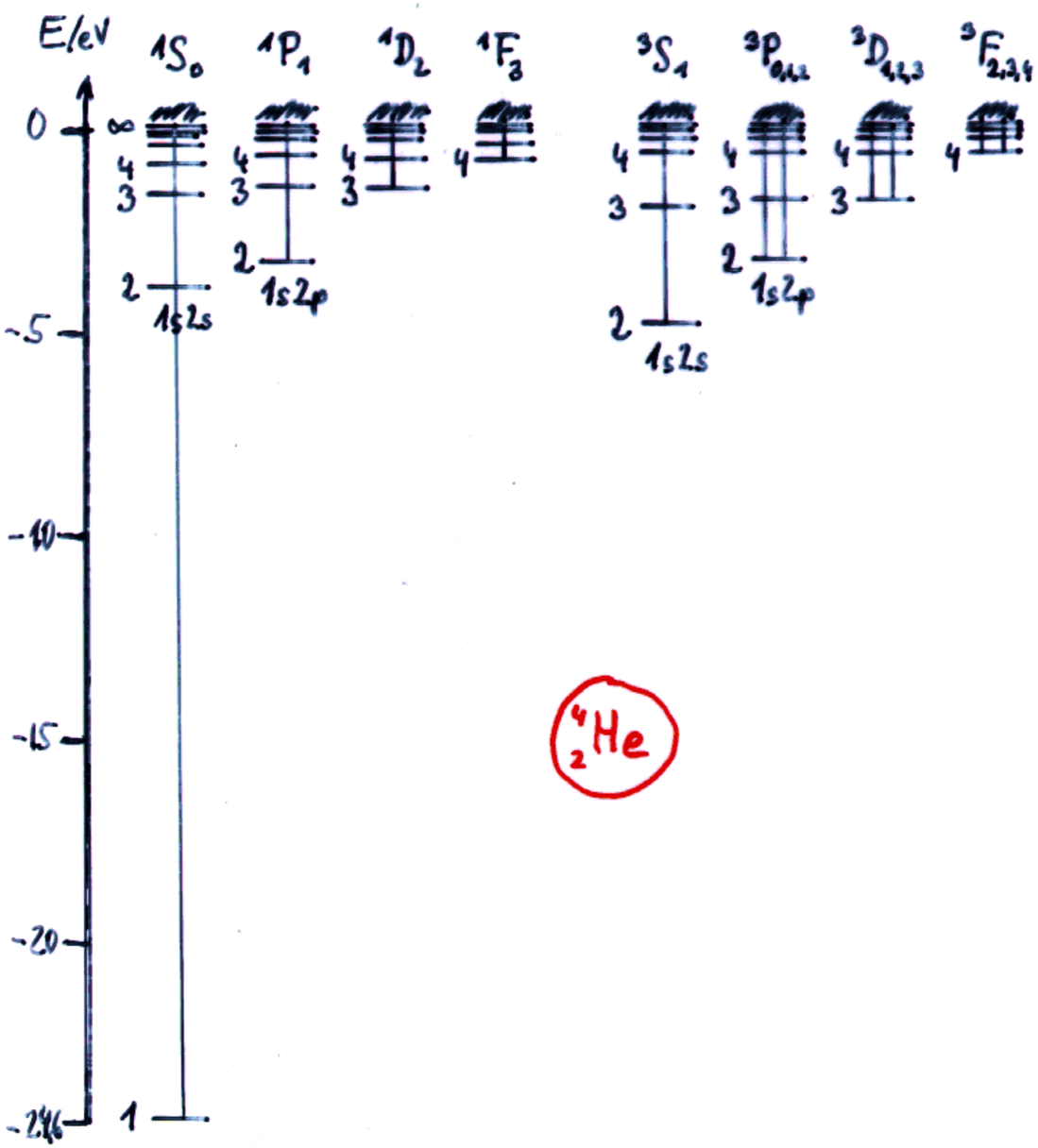


Mehrelektronenatome nicht analytisch.

→ Optimierungsverf. numerisch

→ Quantenchemie / "theoret." Physik

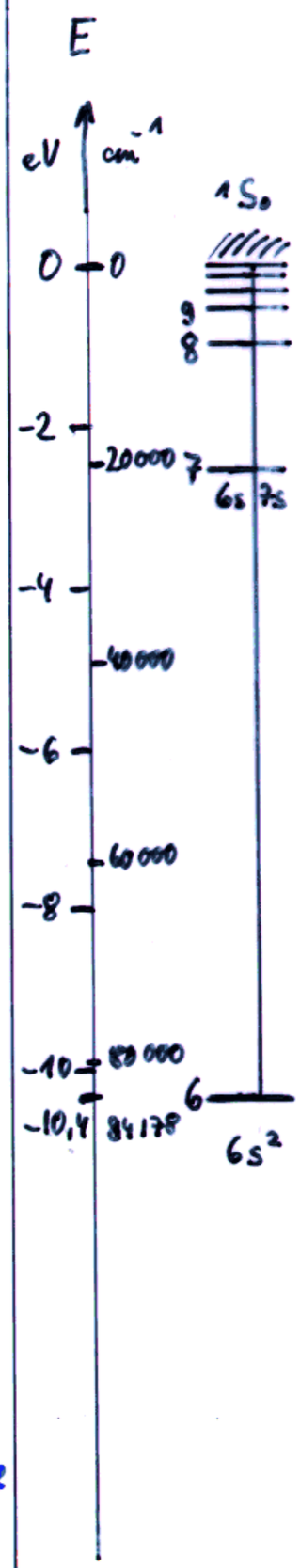
IV/Ma



^4_2He

$1s^2$

Singulett-
"Para helium"



Triplett-Zustände
"Ortho helium"

$_{80}Hg$

Hg: $[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2$