Evaluation of Energies of 1s 2s Excited States of Helium

$$\psi_s = \left[\frac{1}{\sqrt{2}}(1s(1)2s(2) + 2s(1)1s(2))\right]\left[\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))\right]$$

$$\psi_s = {}^1\psi_s(r_1,\ r_2)^1\Gamma(\sigma_1,\ \sigma_2)$$

$$\psi_s = \left[\frac{1}{\sqrt{2}}(1s(1)2s(2) - 2s(1)1s(2))\right]\begin{cases}[\alpha(1)\alpha(2)] \\ \left[\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2)\right] \\ [\beta(1)\beta(2)]\end{cases}$$

$$\psi_T = {}^3\psi_T(r_1,\ r_2)^3\Gamma(\sigma_1,\ \sigma_2)$$

$$\langle E\rangle_T^S = \int \psi_{S\,T}^{*}\hat{H}\psi_{S\,T}\,d\tau = \int {}^1{}^3\psi_{S\,T}^{*}\hat{H}\psi_{S\,T}\,dr'' \underbrace{\int \Gamma_{S\,T}^{*}(\sigma_1,\ \sigma_2)\Gamma_{S\,T}(\sigma_1,\ \sigma_2)\,d\sigma_1 d\sigma_2''}_{\|\ 1}$$

$$\langle E\rangle_T^S = \int \psi_{S\,T}^{*}(\hat{H}_1 + \hat{H}_2)\psi_{S\,T}\,dr + \int \psi_{S\,T}^{*}\left(\frac{1}{r_{12}}\right)\psi_{S\,T}\,dr$$

with $\hat{H}_1 1s(1) = E_{1s}1s(1)$ and $\hat{H}_1 2s(1) = E_{2s}2s(1)$, etc.

$$\begin{aligned}\int \psi_{S\,T}^{*}(\hat{H}_1 + \hat{H}_2)\psi_{S\,T}\,dr = \frac{1}{2}\Big\{&\Big[\int 1s^*(1)2s^*(2)(\hat{H}_1 + \hat{H}_2)1s(1)2s(2)\Big]dr_1 dr_2 \\ &\pm\int\Big[1s^*(1)2s^*(2)(\hat{H}_1 + \hat{H}_2)2s(1)1s(2)\Big]dr_1 dr_2 \\ &\pm\int\Big[2s^*(1)1s^*(2)(\hat{H}_1 + \hat{H}_2)1s(1)2s(2)\Big]dr_1 dr_2 \\ &+\int\Big[2s^*(1)1s^*(2)(\hat{H}_1 + \hat{H}_2)2s(1)1s(2)\Big]dr_1 dr_2\Big\}\end{aligned}$$

$$\int \psi^{*}_{\substack{S\\T}}(\hat{H}_1+\hat{H}_2)\psi_{\substack{S\\T}}dr_1dr_2 =$$

$$\frac{1}{2}\Big\{\int 1s^{*}(1)2s^{*}(2)E_{1s}1s(1)2s(2)dr_1dr_2+\int 1s^{*}(1)2s^{*}(2)E_{2s}1s(1)2s(2)dr_1dr_2$$

$$\pm\Big[\int 1s^{*}(1)2s(2)E_{2s}2s(1)1s(2)dr_1dr_2+\int 1s^{*}(1)2s^{*}(2)E_{1s}2s(1)1s(2)dr_1dr_2\Big]$$

$$\pm\Big[\int 2s^{*}(1)1s(2)E_{1s}1s(1)2s(2)dr_1dr_2+\int 2s^{*}(1)1s^{*}(2)E_{2s}1s(1)2s(2)dr_1dr_2\Big]$$

$$+\int 2s^{*}(1)1s^{*}(2)E_{2s}2s(1)1s(2)dr_1dr_2+\int 2s^{*}(1)1s^{*}(2)E_{1s}2s(1)1s(2)dr_1dr_2\Big\}$$

$$\int \psi^{*}_{\substack{S\\T}}(H_1+H_2)\psi_{\substack{S\\T}}dr=\frac{1}{2}[E_{1s}+E_{2s}\pm 0\pm 0\pm 0\pm 0+E_{2s}+E_{1s}]$$

Why are the integrals for cross terms above zero?

$$\int \psi^{*}_{\substack{S\\T}}(\hat{H}_1+\hat{H}_2)\psi_{\substack{S\\T}}=E_{1s}+E_{2s}$$

$$\left\langle\frac{1}{r_{12}}\right\rangle_{\substack{S\\T}}=\int \psi^{*}_{\substack{S\\T}}\frac{1}{r_{12}}\psi_{\substack{S\\T}}dr_1dr_2$$

$$=\frac{1}{2}\Big[\frac{1s^{*}(1)1s(1)2s^{*}(2)2s(2)}{r_{12}}dr_1dr_2=J$$

$$\pm\int\frac{1s^{*}(1)2s(1)2s^{*}(2)1s(2)}{r_{12}}dr_1dr_2=K$$

$$\pm\int\frac{2s^{*}(1)1s(1)1s^{*}(2)2s(2)}{r_{12}}dr_1dr_2=K$$

$$+\int\frac{2s^{*}(1)2s(1)1s^{*}(2)1s(2)}{r_{12}}dr_1dr_2=J\Big]$$

$$\langle E\rangle^{S}_{T}=E_{1s}+E_{2s}+\frac{1}{2}[2J\pm 2K]=E_{1s}+E_{2s}+J\pm K$$

since $K>0$ $\quad\langle E\rangle_{s}>\langle E\rangle_{T}$