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

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

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

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

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

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

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

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

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

$$\int \psi^*_{\substack{S\\T}}(\hat{H}_1 + \hat{H}_2)\psi_{\substack{S\\T}} dr_1 dr_2 =$$

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

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

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

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

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

Why are the integrals for cross terms above zero?

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

$$\left\langle \frac{1}{r_{12}} \right\rangle_{\substack{S\\T}} = \int \psi^*_{\substack{S\\T}} \frac{1}{r_{12}} \psi_{\substack{S\\T}} dr_1 dr_2$$

$$= \frac{1}{2}\Big[\int \frac{1s^*(1)1s(1)2s^*(2)2s(2)}{r_{12}} dr_1 dr_2 = J$$

$$\pm\int \frac{1s^*(1)2s(1)2s^*(2)1s(2)}{r_{12}} dr_1 dr_2 = K$$

$$\pm\int \frac{2s^*(1)1s(1)1s^*(2)2s(2)}{r_{12}} dr_1 dr_2 = K$$

$$+\int \frac{2s^*(1)2s(1)1s^*(2)1s(2)}{r_{12}} dr_1 dr_2 = J\Big]$$

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

since $K > 0$ $\qquad \langle E\rangle_s > \langle E\rangle_T$.