15.7: Appendix

Triplets. A triplet wavefunction is defined by the Slater determinate: $\Psi^3(1,2) =$

```
det\frac{1}{\sqrt{2}}\left|{\mathit{\Psi}}_1\left(1\right)\alpha \left(1\right)\ {\mathit{\Psi}}_1\left(2\right)\alpha \left(2\right)\ {\mathit{\Psi}}_2\left(1\right)\alpha \left(1\right)\ {\mathit{\Psi}}_2\left(2\right)\alpha \left(2\
```

We now apply this to the electron-electron repulsion operator $\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}$ as follows:

\[\int{}

ParseError: invalid DekiScript (click for details)

^3\left(1,2\right)\cdot \partial \tau = \nonumber \]

$$\int \{\psi_1^*(1)\alpha^*(1)\psi_2^*(2)\alpha^*(2) - \psi_2^*(1)\alpha^*(1)\psi_1^*(2)\alpha^*(2)\}\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\{\Psi_1(1)\alpha(1)\Psi_2(2)\alpha(2) - \Psi_2(1)\alpha(1)\Psi_1(2)\alpha(2)\}\cdot\partial\tau$$

Next the expression is FOIL'ed out and the spin wavefunctions are factored out:

\[\frac{1}{2}\int{}{\psi }^*_1\left(1\right){\mathit{\Psi}}_1\left(1\right)\frac{e^2}{4\pi {\varepsilon }_0\left|r_1-r_2\right|}

ParseError: invalid DekiScript (click for details)

_2\left(2\right)\cdot \partial \tau \int{}{\alpha }^*\left(1\right)\alpha \left(1\right)\int{}{\alpha }^*\left(2\right)\alpha \left(2\right)+\frac{1}{2}\int{}{\mathit{\Psi}}^*_1\left(2\right){\mathit{\Psi}}_1\left(2\right)\frac{e^2}{4\pi {\varepsilon }_0\left|r_1-r_2\right|}{\mathit{\Psi}}^*_2\left(1\right){\mathit{\Psi}}_2\left(1\right)\cdot \partial \tau \int{}{\alpha }^*\left(1\right)\alpha \left(1\right)\int{}{\alpha }^*\left(2\right)\alpha \left(2\right)-\frac{1}{2}\int{}{\mathit{\Psi}}^*_1\left(1\right){\mathit{\Psi}}_1\left(2\right)\frac{e^2}{4\pi {\varepsilon }_0\left|r_1-r_2\right|}{\mathit{\Psi}}^*_2\left(2\right){\mathit{\Psi}}_2\left(1\right)\cdot \partial \tau \int{}{\alpha }^*\left(1\right)\alpha \left(1\right)\int{}{\alpha }^*\left(2\right)\alpha \left(2\right)-\frac{1}{2}\int{}{\mathit{\Psi}}^*_1\left(2\right){\mathit{\Psi}}_1\left(1\right)\frac{e^2}{4\pi {\varepsilon }_0\left|r_1-r_2\right|}{\mathit{\Psi}}^*_2\left(1\right){\mathit{\Psi}}_2\left(2\right)\cdot \partial \tau \int{}{\alpha }^*\left(1\right)\alpha \left(1\right)\int{}{\alpha }^*\left(2\right)\alpha \left(2\right) \nonumber \]

Since $\int\alpha^*\alpha = 1$ and $\Psi_1^*(1)\,\Psi_1(1) = |\Psi_1(1)|^2$ etc., the above can be factored into:

$$\frac{1}{2}\left(\int|\Psi_1(1)|^2\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(2)|^2\cdot\partial\tau + \int|\Psi_1(2)|^2\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(1)|^2\cdot\partial\tau\right)$$
$$-\frac{1}{2}\left(\int\Psi_1^*(1)\,\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(2)\,\Psi_2(1)\cdot\partial\tau + \int\Psi_1^*(2)\,\Psi_1(1)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(1)\,\Psi_2(2)\cdot\partial\tau\right)$$

The terms in parentheses are equal because the labels "1" and "2" are arbitrary, and the integral results are the same. The result is the Coulomb integral minus the exchange integral:

\[\int{}

ParseError: invalid DekiScript (click for details)

^3\left(1,2\right)\cdot \partial \tau = \nonumber \]

$$\int|\Psi_1(1)|^2\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(2)|^2\cdot\partial\tau - \int\Psi_1^*(1)\,\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(2)\,\Psi_2(1)\cdot\partial\tau$$

Singlets: A singlet wavefunction is defined by two Slater determinates:

```
det\frac{1}{2}\left(\left|{\mathit{\Psi}}_1\left(1\right)\alpha \left(1\right)\ {\mathit{\Psi}}_1\left(2\right)\alpha \left(2\right)\ {\mathit{\Psi}}_2\left(1\right)\beta \left(1\right)\ {\mathit{\Psi}}_2\left(2\right)\beta \left(2\right
```

$$= \frac{1}{2}\Psi_1(1)\alpha(1)\Psi_2(2)\beta(2) - \frac{1}{2}\Psi_2(1)\beta(1)\Psi_1(2)\alpha(2) - \frac{1}{2}\Psi_1(1)\beta(1)\Psi_2(2)\alpha(2) + \frac{1}{2}\Psi_2(1)\alpha(1)\Psi_1(2)\beta(2)$$

We now apply this to the electron-electron repulsion operator $\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}$ as:

\[\int{}

ParseError: invalid DekiScript (click for details)

^1\left(1,2\right)\cdot \partial \tau \nonumber \]

The expression is FOIL'ed and the spin wavefunctions are factored out on the following page. Since $\int\alpha^*\alpha = 1$, $\int\alpha^*\beta = \int\beta^*\alpha = 0$ and $\psi_1^*(1)\,\Psi_1(1) = |\Psi_1(1)|^2$ etc., half the terms can be removed, and the remainder factored into:

$$\frac{1}{2}\left(\int|\Psi_1(1)|^2\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(2)|^2\cdot\partial\tau + \int|\Psi_1(2)|^2\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(1)|^2\cdot\partial\tau\right)$$
$$+\frac{1}{2}\left(\int\psi_1^*(1)\,\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\psi_2^*(2)\,\Psi_2(1)\cdot\partial\tau + \int\psi_1^*(2)\,\Psi_1(1)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\psi_2^*(1)\,\Psi_2(2)\cdot\partial\tau\right)$$

The terms in parentheses are equal because the labels "1" and "2" are arbitrary. Thus, we have the Coulomb integral plus the exchange integral:

\[\int{}

ParseError: invalid DekiScript (click for details)

^1\left(1,2\right)\cdot \partial \tau = \nonumber \]

$$\int|\Psi_1(1)|^2\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(2)|^2\cdot\partial\tau + \int\Psi_1^*(1)\,\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(2)\,\Psi_2(1)\cdot\partial\tau$$

which proves that the paramagnetic triplet state is lower in energy than the singlet.

\frac{1}{4}\int{}{\mathit{\Psi}}^*_1\left(1\right){\mathit{\Psi}}^*_2\left(2\right)\frac{e^2}{4\pi {\varepsilon }_0\left|r_1-r_2\right|}{\mathit{\Psi}}_1\left(1\right){\mathit{\Psi}}_2\left(2\right)\cdot \partial \tau \int{}{\al