

As for H_2^+ we can build the low-lying states of H_2 from atomic orbitals of 1s hydrogen. The antisymmetric $\psi=\psi_-$, will give us a triplet state:

$$\psi^T \simeq \frac{1}{\sqrt{2}} [\Phi_{1s}(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{B2}) - \Phi_{1s}(\underline{r}_{A2})\Phi_{1s}(\underline{r}_{B1})] \chi^T \quad (19)$$

and the symmetric $\psi=\psi_+$, will give us a singlet state:

$$\psi^S \simeq \frac{1}{\sqrt{2}} [\Phi_{1s}(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{B2}) + \Phi_{1s}(\underline{r}_{A2})\Phi_{1s}(\underline{r}_{B1})] \chi^S \quad (20)$$

As before, to obtain the energy associated to these 2 states we work out expectation value of Hamiltonian, normalized for either singlet or triplet states:

$$E_{\pm}(R) = \frac{\int \psi^{*S,T} \hat{H}_{el} \psi^{S,T} d\tau}{\int \psi^{*S,T} \psi^{S,T} d\tau}$$

$$E_+ \rightarrow \psi^S$$

$$E_- \rightarrow \psi^T$$

Optional: Working through these integrals, like we did for H_2^+ , gives the denominator, $\int \psi^{*S,T} \psi^{S,T} d\tau =$

$$\begin{aligned}
& \frac{1}{2} \int (\Phi_{1s}(r_{A1})\Phi_{1s}(r_{B2}) \pm \Phi_{1s}(r_{A2})\Phi_{1s}(r_{B1}))^* \\
& \times (\Phi_{1s}(r_{A1})\Phi_{1s}(r_{B2}) \pm \Phi_{1s}(r_{A2})\Phi_{1s}(r_{B1})) dr_1 dr_2 \\
& = \frac{1}{2} \int \Phi_{1s}^*(r_{A1})\Phi_{1s}(r_{A1}) dr_1 \int \Phi_{1s}^*(r_{B2})\Phi_{1s}(r_{B2}) dr_2 \\
& + \frac{1}{2} \int \Phi_{1s}^*(r_{A2})\Phi_{1s}(r_{A2}) dr_2 \int \Phi_{1s}^*(r_{B1})\Phi_{1s}(r_{B1}) dr_1 \\
& \pm \frac{1}{2} \int \Phi_{1s}^*(r_{A1})\Phi_{1s}(r_{B1}) dr_1 \int \Phi_{1s}^*(r_{A2})\Phi_{1s}(r_{B2}) dr_2 \\
& \pm \frac{1}{2} \int \Phi_{1s}(r_{A1})\Phi_{1s}^*(r_{B1}) dr_1 \int \Phi_{1s}(r_{A2})\Phi_{1s}^*(r_{B2}) dr_2
\end{aligned} \tag{21}$$

which, remembering that the $\Phi_{1s}(r_{N,i})$ (for $N = A, B$ and $i = 1, 2$) are normalised, and defining the **overlap integral**:

$$I = \int \Phi_{1s}^*(r_{N,i})\Phi_{1s}(r_{M,i}) dr_i \tag{22}$$

we see that:

$$\int \psi^{*S,T} \psi^{S,T} d\tau = 1 \pm I^2 \tag{23}$$

remembering that the ‘+’ corresponds to the spin singlet, and the ‘-’ to the spin triplet.

For the numerator we need to evaluate four parts. First:

$$\int \Phi_{1s}^*(\underline{r}_{A1})\Phi_{1s}^*(\underline{r}_{B2})\hat{H}_{el}\Phi_{1s}(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{B2}) \quad (24)$$

Breaking up \hat{H}_{el} we can identify the $-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}}$ and $-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{B2}}$ as being the hydrogen atom Hamiltonians, and so both will integrate to E_{1s} .

We can also recognise

$$\frac{1}{R} \int |\Phi_{1s}(\underline{r}_{A1})|^2 |\Phi_{1s}(\underline{r}_{B2})|^2 d\tau = \frac{1}{R} \quad (25)$$

the nuclear repulsion term that was present in the H_2^+ solution.

The rest of the Hamiltonian gives rise to:

$$\int |\Phi_{1s}(\underline{r}_{A1})|^2 |\Phi_{1s}(\underline{r}_{B2})|^2 d \left(-\frac{1}{r_{B1}} - \frac{1}{r_{A2}} + \frac{1}{r_{12}} \right) d\tau = J(R) \quad (26)$$

which we can identify as a **Coulomb integral** (not exactly the same as in the previous H_2^+ solution)

And so we find the first part of the numerator is

$$2E_{1s} + \frac{1}{R} + J \quad (27)$$

The second term to evaluate is:

$$\int \Phi_{1s}^*(\underline{r}_{A2})\Phi_{1s}^*(\underline{r}_{B1})\hat{H}_{el}\Phi_{1s}(\underline{r}_{A2})\Phi_{1s}(\underline{r}_{B1}) \quad (28)$$

which, as only the electron number labels have changed clearly integrates to the same as the above.

The third term is a ‘cross term’:

$$\int \Phi_{1s}^*(\underline{r}_{A2})\Phi_{1s}^*(\underline{r}_{B1})\hat{H}_{el}\Phi_{1s}(\underline{r}_{A1})\Phi_{1s}(\underline{r}_{B2}) \quad (29)$$

Adopting the same procedure as above, the first part we tackle is the hydrogen atom Hamiltonians $-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}}$ and $-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{B2}}$ which will produce two terms equal to

$$\pm E_{1s}I^2 \quad (30)$$

where I is the overlap as defined before which occurs because we now have to evaluate terms like $\int \Phi^*(\underline{r}_{B1})\Phi(\underline{r}_{A1})d\mathbf{r}_1$.

We can also identify the nuclear repulsion term:

$$\pm \frac{1}{R}I^2 \quad (31)$$

remembering the ‘+’ and ‘-’ are spin singlet and triplet respectively.

This leaves only the part:

$$\int \Phi^*(\underline{r}_{A2})\Phi^*(\underline{r}_{B1})\Phi(\underline{r}_{A1})\Phi(\underline{r}_{B2}) \left(-\frac{1}{r_{B1}} - \frac{1}{r_{A2}} + \frac{1}{r_{12}} \right) d\tau \quad (32)$$

which we will denote $K(R)$, the **Exchange Integral**.

So the contribution from this third term is

$$\pm(2E_{1s} + \frac{1}{R})I^2 + K \quad (33)$$

The fourth term is the other cross-term, which again differs only by the electron labels being swapped, and so integrates to the same result.

Adding together all four terms (and remembering the factor of $\frac{1}{2}$ from the initial normalisation), we get:

$$\langle \psi^{S,T} | \hat{H}_{el} | \psi^{S,T} \rangle = (2E_{1s} + \frac{1}{R})(1 + I^2) + J \pm K \quad (34)$$

where the sign of K depends on the symmetry of the wavefunction.

Normalising we find an expression for the energy:

$$E_{\pm} = 2E_{1s} + \frac{1}{R} + \frac{J}{1 \pm I^2} \pm \frac{K}{1 \pm I^2} \quad (35)$$