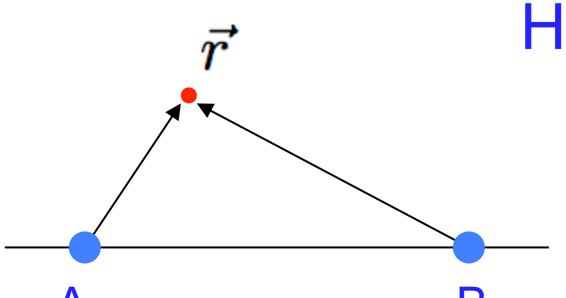
H_2^+ molecular orbitals



Hamiltonian for one electron

$$\mathcal{H} = \frac{\hat{\vec{p}}^{\,2}}{2m} - \frac{e^2}{|\hat{\vec{r}} - \vec{R}_A|} - \frac{e^2}{|\hat{\vec{r}} - \vec{R}_B|}$$

Ansatz for wavefunction through linear combination of atomic orbitals

$$\psi(\vec{r}) = c_A \phi_A(\vec{r}) + c_A \phi_B(\vec{r})$$

$$\phi_{A,B}(\vec{r}) = \phi_{1s}(\vec{r} - \vec{R}_{A,B})$$

even / odd parity states

$$\psi_\pm(\vec{r}) = C_\pm \left[\phi_A(\vec{r}) \pm \phi_B(\vec{r})\right]$$

$$\begin{cases} C_\pm = [2(1 \pm \alpha)]^{-1/2} \\ \alpha = \int d^3r \, \phi_A(\vec{r})^* \phi_B(\vec{r}) \end{cases}$$

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energy (variational)

$$\mathcal{H} = \frac{\hat{\vec{p}}^{\,2}}{2m} - \frac{e^2}{|\hat{\vec{r}} - \vec{R}_A|} - \frac{e^2}{|\hat{\vec{r}} - \vec{R}_B|}$$

$\rightarrow$

$$\epsilon_\pm = \int d^3r \, \psi_\pm(\vec{r})^* \mathcal{H} \psi_\pm(\vec{r})$$

$$\epsilon_\pm = \langle \mathcal{H} \rangle_{AA} + \langle \mathcal{H} \rangle_{BB} \pm \langle \mathcal{H} \rangle_{AB} \pm \langle \mathcal{H} \rangle_{BA}$$

$$= 2\langle \mathcal{H} \rangle_{AA} \pm 2\langle \mathcal{H} \rangle_{AB}$$

$$\langle \mathcal{H} \rangle_{AA} = \frac{E_{1s} + \Delta E}{2(1 \pm \alpha)}$$

$$\langle \mathcal{H} \rangle_{AB} = \frac{\alpha E_{1s} + \gamma}{2(1 \pm \alpha)}$$

$$E_{1s} = \int d^3r \, \phi_{1s}(\vec{r}) \left\{ \frac{\hat{\vec{p}}^{\,2}}{2m} + \frac{e^2}{|\vec{r}|} \right\} \phi_{1s}(\vec{r})$$

$$\Delta E = \int d^3r \, \phi_A(\vec{r}) \frac{e^2}{|\vec{r} - \vec{R}_B|} \phi_A(\vec{r})$$

$$\gamma = \int d^3r \, \phi_A(\vec{r}) \frac{e^2}{|\vec{r} - \vec{R}_B|} \phi_B(\vec{r})$$

$$\epsilon_\pm = E_{1s} + \frac{\Delta E \pm \gamma}{1 \pm \alpha}$$