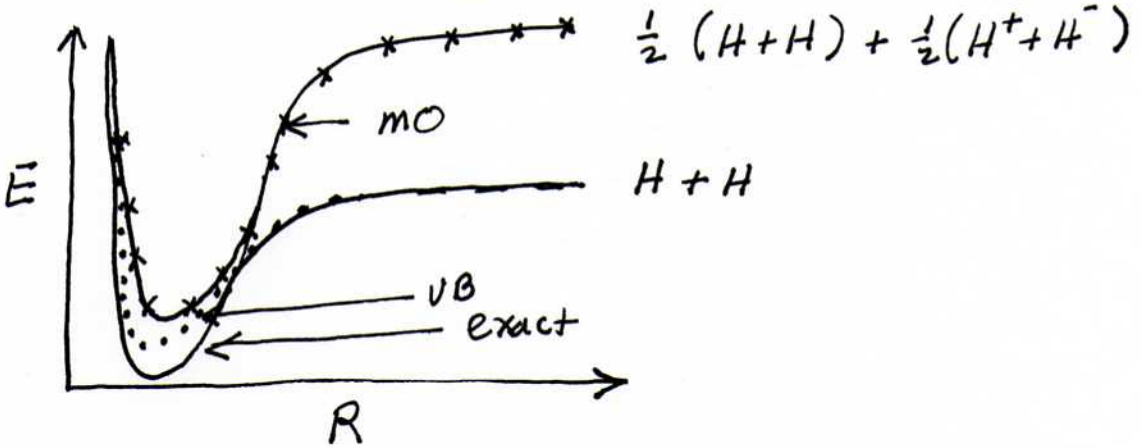
H_2 valence-bond (VB) $\psi \sim (1s_a 1s_b + 1s_b 1s_a)(\alpha\beta - \beta\alpha)$

molecular orbital (MO) $\psi \sim \sigma_g \sigma_g (\alpha\beta - \beta\alpha)$

$$\sigma_g(1)\sigma_g(2) = (1s_a + 1s_b)(1s_a + 1s_b) =$$

$$\underbrace{(1s_a^2 + 1s_b^2)}_{\text{ionic}} + \underbrace{(1s_a 1s_b + 1s_b 1s_a)}_{\text{covalent}}$$



MO unrealistic in its dissociation ($R \to \infty$) limit
VB dissociates correctly, but does not include any ionic character for $R \approx R_e$

$$E^{VB} = 2E_{1s} + \frac{J + K}{1 + S_{ab}^2}$$

$$J = -\langle 1s_a 1s_b | \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}}\right) | 1s_a 1s_b \rangle$$

$$K = -\langle 1s_a 1s_b | \left(\frac{1}{r_{a_2}} + \frac{1}{r_{b_1}} - \frac{1}{r_{12}}\right) | 1s_b 1s_a \rangle$$

How to improve on the MO result

$$\psi = c_1 1\sigma_g^2 + c_2 1\sigma_u^2 \to c_1(a+b)^2 + c_2(a-b)^2$$

$$= c_1[a^2 + b^2 + (ab + ba)] + c_2[a^2 + b^2 - (ab + ba)]$$

$R \to \infty$
$c_1 = -c_2$