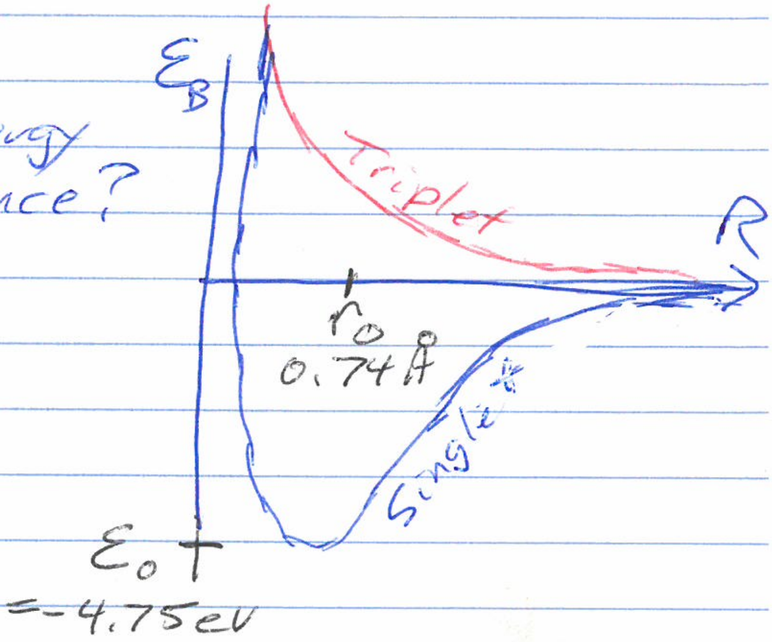
Chemical Bonds, Magnetic Interactions, & 'Exchange' Forces: Molecular H_2

How does H_2 energy vary with distance?

$\mathcal{E}_B = \mathcal{E}(R) - \mathcal{E}(\infty)$
chemical bond strength



- Singlet vs. Triplet

Q: For small r, what is the electronic ground state spin & energy?

A: Small r = He!

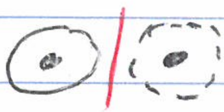
$\mathcal{E}_B = \mathcal{E}_{S=0} = -78.95\,eV + \frac{e^2}{r}$

$\mathcal{E}_{AB} = \mathcal{E}_{S=1} = -59.13\,eV + \underbrace{e^2/r}_{\text{Nuclear repulsion}}$ } Net repulsion

$(\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$

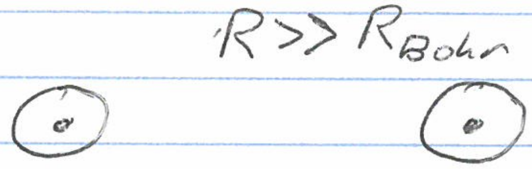
Singlet = "Bonding" $\mathcal{E}_B$

Triplet = "Antibonding" = $\mathcal{E}_{AB}$



Node from Antisymmetry → Repels

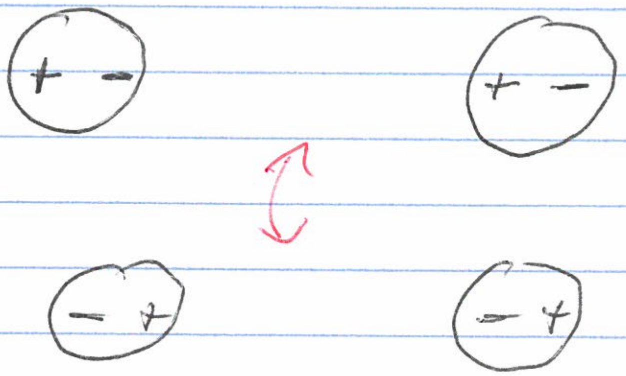
- Van der Waals



Q: What is the variational energy of two H atom ground states, for $R \gg R_{bohr}$ (neglecting overlaps).

A: Spherical charge clouds – no net Coulomb. No overlap → $E = 0$.

Dominant interaction at long distances, neutral atoms from quantum charge fluctuations –



Polarizations correlate to lower energy.

Calculation not done here,

$$V_{\text{Van der Waals}}(r) \sim \frac{[\text{Polarizability}]^2}{r^6}$$

Dominates attraction

- for closed-shell atoms (He, Ne, Ar...) and non-polar molecules (CH_4)

- Magnetic interactions between electron spins

Q: What is the interaction energy between electron spins in H_2?

A: Trick question.

<u>Direct</u> interaction between magnetic dipoles (SI units) $m = -g \frac{\mu_B}{\hbar} S \approx \mu_B$

$(S = \hbar/2,\ g \approx 2)$

$$\boxed{\begin{array}{ll} \uparrow\ \downarrow & \frac{\mu_0}{4\pi r^3} m^2 \\ \rightarrow\ \rightarrow & \frac{2\mu_0}{4\pi r^3} m^2 \end{array}}$$

$r = 1\,\mathring{A} = 10^{-10}\,m$

$$\frac{\mu_0 \mu_B}{4\pi r^3} = \frac{\left(4\pi \times 10^{-7} \frac{T m s^2}{kg}\right)\left(9.28 \times 10^{-24}\, J/T\right)^2}{4\pi \left(10^{-10}\, m\right)^3 \left(1.6 \times 10^{-19}\, J/eV\right)}$$

$$= 5.4 \times 10^{-5}\, eV$$

too small to matter.

"<u>Exchange</u>" force =

= Effective force between spins <u>due</u> to $E_{triplet} - E_{singlet}$

$\approx 5\,eV$ preference for $S_{TOT} = 0$ vs. $S_{TOT} = 1$

- "Exchange" Force

Effective Hamiltonian between spins

$$\mathcal{H}_{eff} = \begin{cases} E_B, & S_{TOT} = 0 \quad (\text{singlet}) \\ E_{AB}, & S_{tot} = 1 \quad (\text{triplet}) \end{cases}$$

$$S^2 = S(S+1) = \begin{cases} 0 & S = 0 \\ 2\hbar^2 & S = 1 \\ 3/4\,\hbar^2 & S = 1/2 \end{cases} \qquad S_{TOT} = S_1 + S_2$$

$$\mathcal{H}_{eff} = E_B + (E_{AB} - E_B)\frac{(\vec{S}_1 + \vec{S}_2)}{2\hbar^2}$$

$$= E_B + \frac{E_{AB} - E_B}{2\hbar^2}\Big(\underbrace{\vec{S}_1^{\,2} + \vec{S}_2^{\,2}}_{3/2\,\hbar^2} + 2\vec{S}_1 \cdot \vec{S}_2\Big)$$

$$= \underbrace{E_B + \frac{3}{4}(E_{AB} - E_B)}_{\text{Boring}} + \underbrace{\frac{E_{AB} - E_B}{\hbar^2}}_{-J/2\hbar^2}\vec{S}_1 \cdot \vec{S}_2$$

For H_2, $J < 0$ antiferromagnetic (wants spins antiparallel)

For iron (more complicated calculation) $J > 0$ $\underbrace{\text{ferro}}_{\text{like iron}}$magnetic, parallel.

Note! More typical convention: $\vec{S} = \pm 1/2$,
J

- Why is it called the <u>exchange</u> interaction?

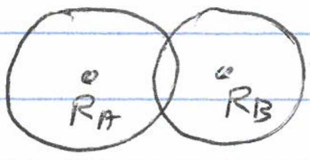
Heitler-London Approximation

- Not a good estimate
- Conyers Herring (1965) "thorough critique"
- Ashcroft & Mermin (1976)"
  "source of a nomenclature that pervades much of the subject of magnetism"

At medium-long distances, treat

$$\Psi_{\pm} = \frac{1}{\sqrt{2}}\Big(\underbrace{\phi_0(r_1-R_A)}_{\phi_A}\ \underbrace{\phi_0(r_2-R_B)}_{\phi_B} \pm \phi_0(r_2-R_A)\phi_0(r_1-R_B)\Big)$$

$\phi_0 \equiv$ H ground state wave function.



Overlapping electron clouds.

- Nonorthogonality → ugly.
- Electrons 'feel' other nucleus
- $$\frac{E_t - E_s}{2} \simeq \iint \overset{\frac{e^2}{|r_1-r_2|}+\frac{e^2}{(r_1-R_A)}+\dots}{u}\ \underbrace{\phi_A(r_1)\,\phi_A^*(r_2)\,\phi_B(r_2)\,\phi_B^*(r_1)}_{\text{'Exchange' of } r_1, r_2 \text{ between atoms}}\,dr_1 dr_2$$