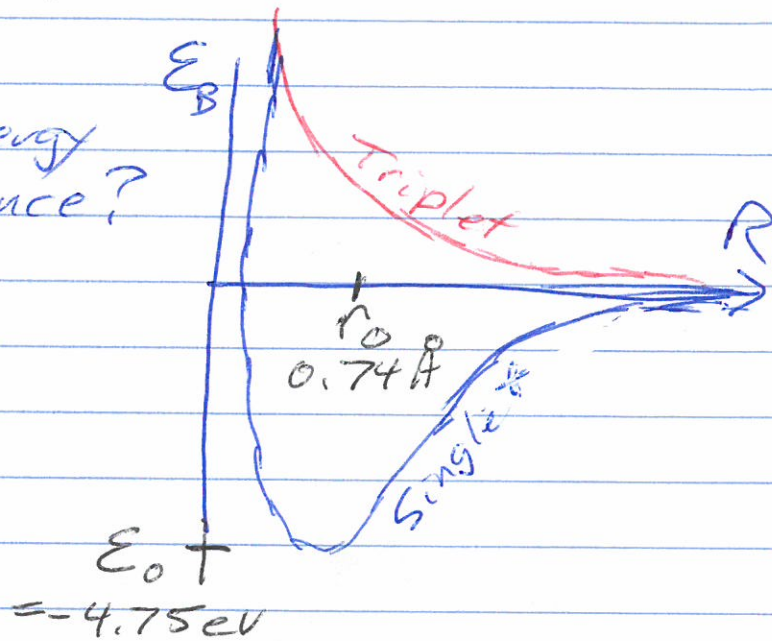


Chemical Bonds, Magnetic Interactions, & 'Exchange' Forces: Molecular H₂

How does H₂ energy vary with distance?

$E_B = E(R) - E(\infty)$
chemical bond strength



• Singlet vs. Triplet

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

A: Small $r = \text{He!}$

$E_B = E_{S=0} = -78.95 \text{ eV} + \frac{e^2}{r}$

$E_{AB} = E_{S=1} = -59.13 \text{ eV} + \frac{e^2}{r}$ } Net repulsion

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

⊙ ⊙ Singlet = "Bonding" E_B Nuclear repulsion

Triplet = "Antibonding" = E_{AB}

⊙ | ⊙ Node from Antisymmetry → Repels

Bonds (2)

• Van der Waals

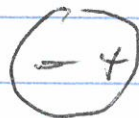
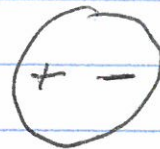
$$R \gg R_{\text{Bohr}}$$

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



A: Spherical charge clouds - no net Coulomb. No overlap $\rightarrow E=0$.

Dominant interaction at long distances, neutral atoms
From quantum charge fluctuations



Polarizations correlate to lower energy.

Calculation not done here,

$$V(r) \sim \frac{[\text{Polarizability}]^2}{r^6}$$

Dominates attraction

• For closed-shell atoms (He, Ne, Ar...) and non-polar molecules (CH₄)

- Magnetic interactions between electron spins

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

A: Trick question.

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

($s = \frac{1}{2}$, $g \approx 2$)

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

$$r = 1 \text{ \AA} = 10^{-10} \text{ m}$$

$$\begin{aligned} \frac{\mu_0 \mu_B}{4\pi r^3} &= \frac{(4\pi \times 10^{-7} \frac{T \cdot m \cdot s^2}{kg}) (9.28 \times 10^{-24} \frac{J}{\hbar})^2}{4\pi (10^{-10} \text{ m})^3 (1.6 \times 10^{-19} \text{ J/eV})} \\ &= 5.4 \times 10^{-5} \text{ eV} \end{aligned}$$

too small to matter.

"Exchange" Force =

= Effective force between spins
due to $E_{\text{triplet}} - E_{\text{singlet}}$

$\approx 5 \text{ eV}$ preference for $S_{\text{tot}} = 0$ vs. $S_{\text{tot}} = 1$

• "Exchange" Force

Effective Hamiltonian between spins

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

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

$$\begin{aligned} H_{\text{eff}} &= E_B + (E_{AB} - E_B) \frac{(\vec{S}_1 + \vec{S}_2)^2}{2\hbar^2} \\ &= E_B + \frac{E_{AB} - E_B}{2\hbar^2} \left(\underbrace{S_1^2 + S_2^2}_{\frac{3}{4}\hbar^2} + 2\vec{S}_1 \cdot \vec{S}_2 \right) \\ &= \underbrace{E_B + \frac{3}{4}(E_{AB} - E_B)}_{\text{Boring}} + \underbrace{\frac{E_{AB} - E_B}{\hbar^2}}_{-J/2\hbar} \vec{S}_1 \cdot \vec{S}_2 \end{aligned}$$

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

For iron (more complicated calculation)
 $J > 0$ ferromagnetic, parallel.
like iron

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

- Why is it called the exchange interaction?

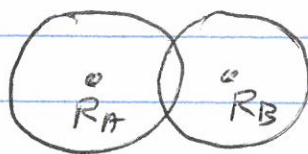
Heitler-London Approximation

- 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

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

ϕ_0 = ground state wave function,



Overlapping electron clouds,

- Nonorthogonality \rightarrow ugly,
- Electrons 'feel' other nucleus

$$\frac{E_6 - E_5}{2} \approx \iint U \underbrace{\phi_A(r_1) \phi_A^*(r_2) \phi_B(r_2) \phi_B^*(r_1)}_{\text{'Exchange' of } r_1, r_2 \text{ between atoms}} dr_1 dr_2$$

'Exchange' of r_1, r_2 between atoms