

Basic properties 2

### Magnetism, why bother?

- Up to now only terribly weak effects:  $\chi = 10^{-4} \ll 1$
- Collective coupling of spins leads to strong magnetic moments that often can be detected directly but even more commonly leads to hidden order: antiferromagnets

Ferromagnets		Elements: Fe, Co, Ni, Gd Alloys: Permalloy FeNi
Antiferromagnets		Elements: Cr, Oxides: MnO, NiO, HTSc
Ferrimagnets		Oxides: Fe <sub>2</sub> O <sub>3</sub> , Gd <sub>3</sub> Fe <sub>5</sub> O <sub>14</sub> RE/TM: ErCo <sub>5</sub> , Dy <sub>2</sub> Fe <sub>14</sub> B

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### The Exchange Interaction

- Central for understanding magnetic interactions in solids
- Arises from *Coulomb* electrostatic interaction and the *Pauli* exclusion principle

Coulomb repulsion-energy high

Coulomb repulsion-energy lowered

$$U_c = \frac{e^2}{4\pi\epsilon_0 r^2} \sim 10^{-18} \text{ J} \quad (10^5 \text{ K!})$$

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### Exchange energy

Wave function of two electrons must be antisymmetric for exchange of particles

$$\psi(r_1, s_1; r_2, s_2) = -\psi(r_2, s_2; r_1, s_1)$$

Chance that two electrons with same spin are at the same place is zero.  
→ Pauli principle takes care that parallel spins avoid each other.

Electron density around each electron in free electron gas (Ibach and Lüth)

Exchange correlation gap radius:  $r = 2/k_F \sim 1-2\text{\AA}$

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### Exchange energy

Consequences from exchange correlation:

Antiparallel spins (singlet state) have lower Coulomb energy than parallel spins (triplet state)

$$\Delta E_{\text{exchange}} = -2J s_1 \cdot s_2$$

**J** Exchange energy

See Ibach/Lüth

$$E_t - E_s = 2 \frac{CS - A}{1 - S^2} = -J$$

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### Heisenberg Hamiltonian

Heisenberg Hamiltonian for lattice:

$$H = - \sum_i \sum_{j \neq i} 2J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

i over all atoms  
j over the neighbor atoms

**Ferromagnetic coupling for positive J**  
**Antiferromagnetic coupling for negative J**

What does this mean?

- Electrons on same atom preferring parallel spins (Hund's rules/atomic correlations):  $J > 0$
- Binding often results in antiparallel spins on neighbor atoms:  $J < 0$  (1 reason why not so many ferromagnetic materials exist)

Heisenberg Hamiltonian is a good starting point for theories for magnetic materials with predominant neighbor interactions (e.g. isolator)

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### Fe spin resolved

Fe-BCC Spin-polarized  $a=5.41 \text{ \AA}$ .

Magnetic moment:  $4.8 - 2.6 = 2.2 \mu_B$

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### Properties of ferromagnets

Not only whole or half integer moments

Material	$T_c$ (K)	Spontaneous magnetization ( $\mu_B$ per atom) at $T = 0$	Theory	
			$gJ$	$2S$
Fe	1043	2.22	Fe <sup>3+</sup> 5	5
Co	1388	1.72	Fe <sup>2+</sup> 6	4
Ni	627	0.61	6	3
Gd	292	7.63	5	2
Dy	88	10.2	7	-
EuO	69	6.8	10	-
			7	-

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### Heisenberg Hamiltonian

$$E_t - E_s = 2 \frac{CS - A}{1 - S^2} = -J$$

Heisenberg model Hamiltonian

$$H = -\sum_i \sum_{j \neq i} 2J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

Ferromagnetic coupling for positive  $J$   
Antiferromagnetic for negative  $J$

- Electrons on the same atom can have parallel spins (Hund's rules/atomic correlations)
- Bonding tends to lead to antiparallel moments on neighboring atoms (one reason why there are not many magnetic compounds)
- But if  $J$  is positive neighboring atom moments couple parallel
- Heisenberg Hamiltonian is good starting point for many theories on magnetism for systems with only pair wise interactions

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### I&L8.3 Exchange interaction between Free Electrons

- Free electron wavefunction  $\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$
- Two free electron pair wavefunction
 
$$\psi_{ij}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_i \cdot \mathbf{r}_i} e^{i\mathbf{k}_j \cdot \mathbf{r}_j}$$
- space antisymmetric:
 
$$\psi_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{\sqrt{2V}} \left( e^{i\mathbf{k}_i \cdot \mathbf{r}_i} e^{i\mathbf{k}_j \cdot \mathbf{r}_j} - e^{i\mathbf{k}_j \cdot \mathbf{r}_i} e^{i\mathbf{k}_i \cdot \mathbf{r}_j} \right)$$

$$\psi_{ij}(\mathbf{r}_i - \mathbf{r}_j) = \frac{1}{\sqrt{2V}} e^{i(\mathbf{k}_i \cdot \mathbf{r}_i + \mathbf{k}_j \cdot \mathbf{r}_j)} \left( 1 - e^{i(\mathbf{k}_i - \mathbf{k}_j) \cdot (\mathbf{r}_i - \mathbf{r}_j)} \right)$$

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### Exchange interaction between Free Electrons

$$\psi_{ij}(\mathbf{r}_i - \mathbf{r}_j) = \frac{1}{\sqrt{2V}} e^{i(\mathbf{k}_i \cdot \mathbf{r}_i + \mathbf{k}_j \cdot \mathbf{r}_j)} \left( 1 - e^{i(\mathbf{k}_i - \mathbf{k}_j) \cdot (\mathbf{r}_i - \mathbf{r}_j)} \right)$$

- Probability of finding electron 1 in  $d\mathbf{r}_1$  and electron 2 in  $d\mathbf{r}_2$ :
 
$$|\psi_{ij}(\mathbf{r}_i - \mathbf{r}_j)|^2 d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{V^2} [1 - \cos(\mathbf{k}_i - \mathbf{k}_j) \cdot (\mathbf{r}_i - \mathbf{r}_j)] d\mathbf{r}_1 d\mathbf{r}_2$$
- Two electrons with same spin cannot be at same position
- Ionic charge of a spin-up electron is not screened by other spin-up electrons.
- This lowers the energy and leads to a **collective exchange interaction with positive sign**

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### Exchange hole

Exchange interaction causes each spin to push away other spins  
→ local charge density modified: **Exchange hole**

up electrons only:

$$\rho_{ex}(\mathbf{r}) = \frac{en}{2} \left( 1 - 9 \frac{(\sin k_F r - \cos k_F r)^2}{(k_F r)^6} \right)$$

All electrons

$$\rho_{ex}(\mathbf{r}) = en \left( 1 - \frac{9}{2} \frac{(\sin k_F r - \cos k_F r)^2}{(k_F r)^6} \right)$$

radius  $r = 2/k_F \sim 1-2\text{\AA}$

Use this density in Schrödinger equation: **Hartree-Fock approximation**.

Full theory  
Density Functional theory in Local Density Approximation (DF-LDA)

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### Band (Stoner) Model of ferromagnetism

Heisenberg model does not completely explain ferromagnetism in metals.

$$E_{\uparrow}(k) = E(k) - \frac{I_s n_{\uparrow}}{N}$$

$$E_{\downarrow}(k) = E(k) - \frac{I_s n_{\downarrow}}{N}$$

$I_s$  is Stoner parameter and describes energy reduction due to electron spin correlation

$n_{\uparrow}, n_{\downarrow}$  is density of up, down spins

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**Band (Stoner) Model**

$$R = \frac{n_{\uparrow} - n_{\downarrow}}{N} \quad (\text{spin excess}) \quad M = \mu_B \frac{N}{V} R$$

Then  $E_{\uparrow}(k) = \tilde{E}(k) - I_s R / 2$   
 $E_{\downarrow}(k) = \tilde{E}(k) + I_s R / 2$        $\tilde{E}(k) = E(k) - \frac{I_s(n_{\uparrow} + n_{\downarrow})}{2N}$

Spin excess given by Fermi statistics:

$$R = \frac{1}{N} \sum_k f_{\uparrow}(k) - f_{\downarrow}(k)$$

$$f_{\uparrow, \downarrow} = \left[ \exp\left(\tilde{E}(k) \mp I_s R / 2 - E_F / kT\right) + 1 \right]^{-1}$$

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**Band (Stoner) Model**

Let R be small, use Taylor expansion:      with  $\Delta x = I_s R$

$$g(x - \Delta x / 2) - g(x + \Delta x / 2) \approx -g'(x)\Delta x - \frac{2}{3!}g'''(x)\left(\frac{\Delta x}{2}\right)^3 + \dots$$

$$R = -\frac{1}{N} \sum_k \frac{\partial f(k)}{\partial \tilde{E}(k)} (I_s R) - \frac{1}{24N} \sum_k \frac{\partial^3 f(k)}{\partial \tilde{E}(k)^3} (I_s R)^3 + \dots$$

$$\sum_k \left( \frac{\partial f}{\partial \tilde{E}} \right) \rightarrow \frac{V}{(2\pi)^3 N} \int dk \left( \frac{\partial f}{\partial \tilde{E}} \right) = \frac{V}{(2\pi)^3 N} \int dk (-\delta(\tilde{E} - E_F))$$

$$= -\frac{V}{2} D(E_F)$$

(at T=0)

D.O.S.: density of states at Fermi level

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**Band (Stoner) Model**

$$\tilde{D}(E_F) = \frac{V}{2N} D(E_F) \quad \text{Density of states per atom per spin}$$

Then  $R = \tilde{D}(E_F) I_s R - O^{(3)}$       Third order terms

$$R(1 - \tilde{D}(E_F) I_s) = -O^{(3)}$$

When is R > 0?

$$1 - \tilde{D}(E_F) I_s < 0 \quad \text{or} \quad \tilde{D}(E_F) I_s > 1$$

Stoner Condition for Ferromagnetism

For Fe, Co, Ni this condition is true

Doesn't work for rare earths, though

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**g(E<sub>F</sub>) and ΔE for a 3d ferromagnet**

1. DOS at Fermi level is greater in a 3d TM:

bandwidth of 3d band smaller (d-d overlap smaller than s-s)  
 band also contains more electrons (can take 10 in total, vs. 2 for 4s band)

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**Spin resolved DOS: 3d ferromagnet**

2. ΔE from alignment with (or against) B<sub>0</sub> is greater in a 3d TM:

**plus:** even a small change in energy, ΔE, leads to a relatively large no. of electrons changing spin state

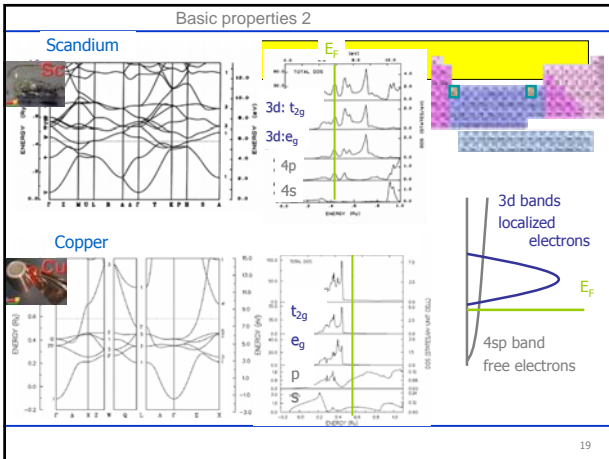
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**Band structure**

Exchange interaction splits spin degenerated bands

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## Susceptibility of ferromagnet

How can we connect the microscopic Heisenberg Hamiltonian with macroscopic properties?

Remark: Magnetization generates non-local effects elsewhere:

Field  $B_{loc}$  at the atom site is the applied field  $B = \mu_0 H$  + the field generated by all the atoms of the magnetic object.

$$B_{loc} = \mu_0 (H_{applied} + H_{nonlocal})$$

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## Weiss molecular field

Pierre Weiss: Exchange interaction of neighboring moments produces molecular field proportional to magnetization

$$B_{Weiss} = \lambda \mu_0 M$$

Weiss field enhances  $B_{loc}$

$$B_{eff} = B_{loc} + \lambda \mu_0 M$$

$$H = - \sum_i \sum_{j \neq i} 2J_{ij} S_i \cdot S_j$$

What is connection between macroscopic  $\lambda$  and microscopic exchange interaction  $J_{ij}$ ?

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## Mean field theory

approximate operator in Hamiltonian with its mean (average) value

Replace  $S_j$  by mean value  $\langle S \rangle$

$$H = - \sum_i \sum_{j \neq i} 2J_{ij} S_i \cdot S_j \Rightarrow H = - \sum_i S_i \sum_{j \neq i} 2J_{ij} \langle S \rangle$$

$\langle S \rangle$  can be expressed in magnetization:

From previous chapter:  $\mu_{eff} = g_L \mu_B S$

Thus magnetization of N atoms

$$M = -Ng \mu_B \langle S \rangle$$

After some operations see gray box p.222 & problem 8.2

$$B_{Weiss} = \lambda \mu_0 M$$

$$\lambda = \frac{2 \sum_{j \neq i} J_{ij}}{N \mu_0 g^2 \mu_B^2}$$

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## Mean Field Theory for disordered phase $T > T_c$

Brillouin function with  $B_{eff}$

$$M(B_{loc}, T) = N \mu_B g J B_J \left( \frac{g \mu_B B_{eff}}{k_B T} \right)$$

Simple case:  $L=0, J=S=1/2, g=2$

$$M(B_{loc}, T) = N \mu_B \tanh \left( \frac{\mu_B B_{eff}}{k_B T} \right)$$

High temperature:  $x \ll 1: \tanh x \rightarrow x$

$$M(B_{loc}, T) = \frac{N \mu_B^2}{k_B T} B_{eff} = \frac{N \mu_B^2}{k_B T} (B_{loc} + \lambda \mu_0 M)$$

Because M is small:  $B_{loc} = \mu_0 H \rightarrow$

Curie-Weiss law

$$\chi_m(T) = \frac{M}{H} = \frac{C}{T - T_c}$$

$C = N \mu_0 \mu_B^2 / k_B$ , Curie temperature:  $T_c = \lambda C$

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## Estimation of exchange interaction

### Curie-Weiss law

$$\chi_m(T) = \frac{M}{H} = \frac{C}{T - T_c}$$

$C = N \mu_0 \mu_B^2 / k_B$

Curie temperature:  $T_c = \lambda C$

For Fe:  $N = 9 \times 10^{28} \text{ m}^{-3} \rightarrow C \sim 1 \text{ K}$

$T_c = 1043 \text{ K} \rightarrow \lambda \sim 1000$

$$\lambda = \frac{2 \sum_{j \neq i} J_{ij}}{N \mu_0 g^2 \mu_B^2} \approx \frac{2zJ}{N \mu_0 g^2 \mu_B^2}$$

$z = 6$  neighbors  $\rightarrow J \sim 30 \text{ meV}$

Material	$T_c$ (K)
Fe	1043
Co	1388
Ni	627
Gd	292
Dy	88
EuO	69

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Mean Field Theory for ordered phase  $T < T_c$

$T < T_c$ : Spontaneous magnetization (also in zero field  $H=0$ )

$$M = N\mu_B \tanh\left(\frac{\mu_B B_{eff}}{k_B T}\right)$$

$$y = \frac{M}{N\mu_B} = \tanh x$$

Assume  $B_{loc}=0$   
(field generated by rest of sample small)

$$B_{eff} = B_{loc} + \lambda\mu_0 M \approx \lambda\mu_0 N$$

$$x = \frac{\mu_B B_{eff}}{k_B T} = \frac{T_c}{T} y$$

Two simultaneous equations for  $y$ . Can only be solved graphically.

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Mean Field Theory for ordered phase  $T < T_c$

$$y = \frac{M}{N\mu_B} = \tanh x \quad x = \frac{\mu_B B_{eff}}{k_B T} = \frac{T_c}{T} y$$

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Failure of Mean Field  $T > T_c$

Mean field theories exclude fluctuations  
→ fails around phase transition:  
critical behavior

$$\chi = (T - T_c)^{-\gamma}$$

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Failure of Mean Field  $T < T_c$

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Beyond mean field

TABLE 8.1 Properties of ferromagnetic materials

Material	$T_c$ (K)	Spontaneous magnetization ( $\mu_B$ per atom) at $T = 0$	Theory		Critical exponents	
			$gJ$	$2S$	$\gamma$	$\beta$
Fe	1043	2.22	$Fe^{3+}$ 5	5	$1.33 \pm 0.02$	$0.34 \pm 0.04$
Co	1388	1.72	$Fe^{2+}$ 6	4	$1.21 \pm 0.04$	-
Ni	627	0.61	5	2	$1.35 \pm 0.02$	$0.42 \pm 0.07$
Gd	292	7.63	7	-	$1.30 \pm 0.10$	-
Dy	88	10.2	10	-	-	-
EuO	69	6.8	7	-	$1.30 \pm 0.01$	$0.36 \pm 0.01$

Mean field  $\gamma = 1$  and  $\beta = 0.5$

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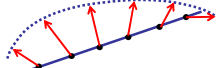
Failure of Mean Field  $T \rightarrow 0$

At low  $T$ : Spinwaves

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### Spin waves

Similar to phonons linear chain 

Energy  $E_n = -2JS_n \cdot (S_{n-1} + S_{n+1})$

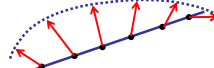
Effective field  $\mathbf{B}_n = -\frac{2J}{g\mu_B} \cdot (S_{n-1} + S_{n+1})$

Equation of motion  $\hbar \frac{d\mathbf{S}_n}{dt} = \boldsymbol{\mu}_n \times \mathbf{B}_n = 2JS_n \times (S_{n-1} + S_{n+1})$

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### Spin waves

Low excitations linearize chain 

$\mathbf{S}_n = -S\mathbf{z} + \boldsymbol{\sigma}_n$

Equation of motion

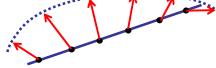
$$\hbar \frac{d\mathbf{S}_n}{dt} = -2JS\mathbf{z} \times (\boldsymbol{\sigma}_{n-1} + \boldsymbol{\sigma}_{n+1}) - 4JS\boldsymbol{\sigma}_n \times \mathbf{z}$$

$$= -2JS\mathbf{z} \times (\boldsymbol{\sigma}_{n-1} - 2\boldsymbol{\sigma}_n + \boldsymbol{\sigma}_{n+1})$$

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### Spin waves

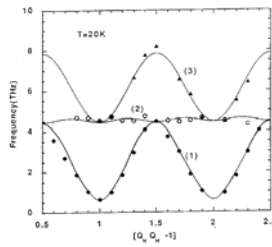
Wave like solutions 

$$\sigma_n = Ae^{i(kna - \omega t)}$$

Dispersion relation

$$\hbar\omega = -2JS(e^{-ika} - 2 + e^{ika}) = 4JS[1 - \cos(ka)]$$

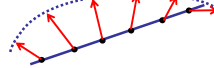
$k \rightarrow 0 \quad \varepsilon = \hbar\omega \approx 2JSa^2k^2$



Spin waves in the antiferromagnet perovskite LaMnO3: A neutron-scattering study\*, Phys. Rev B 54, 15149 (1996) 33

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### Spin waves

Energetics of excitations 

Number of states  $g(k)dk = \frac{Vk^2}{2\pi^2} dk$

Specific heat and magnetization from excitations

$$C = \frac{dE}{dT} = AT^{\frac{3}{2}}$$

$$M = M_s - g\mu_B N = M_s \left[ 1 - BT^{\frac{3}{2}} \right]$$

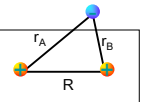
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### H<sub>2</sub><sup>+</sup> ion

#### Tight binding revisited

*single electron*

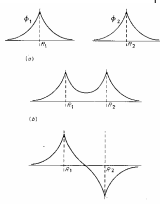
$$H = -\frac{\hbar^2}{2m} \Delta - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R}$$


Try linear combination of atomic orbitals

$$\Psi = C_A\phi_A + C_B\phi_B$$

Perturbation theory gives E'

minimize w.r.t. C<sub>A</sub> & C<sub>B</sub>

$$E' = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau}$$


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### H<sub>2</sub><sup>+</sup> ion

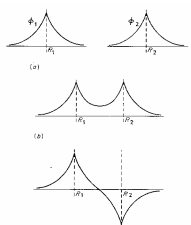
#### Tight binding revisited

$$E' = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau}$$

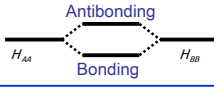
Original energy integral  $H_{AA} = \int \phi_A^* H \phi_A d\tau$

Interaction energy integral  $H_B = \int \phi_A^* H \phi_B d\tau$

Overlap integral  $S = \frac{e^2}{4\pi\epsilon_0} \int \phi_A^* \phi_B d\tau$



$$E_{\pm} \approx \frac{H_{AA} \pm H_{AB}}{1 \pm S}$$

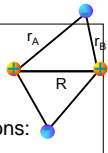


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Exchange Interaction and Bonding

two electrons

$$H(1,2) = H(1) + H(2) + H_{int}(1,2)$$


neglect  $H_{int}$  and try product of atomic wavefunctions:

$$\Psi(1,2) = [\varphi_A(1) + \varphi_B(1)][\varphi_A(2) + \varphi_B(2)]$$

Reasonable simplification: neglect terms with both electrons on same atom  $\rightarrow$  Heitler London wavefunction:

$$\Psi(1,2) = \varphi_A(1)\varphi_B(2) + \varphi_B(1)\varphi_A(2)$$

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H<sub>2</sub> molecule Basic properties 2

Symmetry requirement of wavefunction

$$\Psi(1,2) = \varphi_A(1)\varphi_B(2) + \varphi_B(1)\varphi_A(2)$$

Space part **symmetric** for exchange of (1) and (2)

$\rightarrow$  spin part antisymmetric: **spin singlet S=0**  $|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle$

$$\Psi(1,2) = \varphi_A(1)\varphi_B(2) - \varphi_B(1)\varphi_A(2)$$

Space part **asymmetric** for exchange of (1) and (2)

$\rightarrow$  spin part symmetric: **spin triplet S=1**  $|\uparrow\uparrow\rangle$   
 $|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$   
 $|\downarrow\downarrow\rangle$

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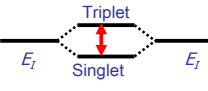
H<sub>2</sub> molecule Basic properties 2

Exchange Interaction

Perturbation theory gives

$$E = 2E_i + \frac{C \pm A}{1 \pm S}$$

+ for singlet  
- for triplet



**C: Coulomb integral**

$$C = \frac{e^2}{4\pi\epsilon_0} \int \left( \frac{1}{R_{AB}} + \frac{1}{r_{12}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} \right) \varphi_A(1)^2 \varphi_B(2)^2 d\tau_1 d\tau_2$$

**A: Exchange integral**

$$A = \frac{e^2}{4\pi\epsilon_0} \int \left( \frac{1}{R_{AB}} + \frac{1}{r_{12}} - \frac{1}{r_{A1}} - \frac{1}{r_{B2}} \right) \varphi_A^*(1)\varphi_A(2)\varphi_B(1)\varphi_B^*(2) d\tau_1 d\tau_2$$

**S: Overlap integral**

$$S = \frac{e^2}{4\pi\epsilon_0} \int \varphi_A^*(1)\varphi_A(2)\varphi_B(1)\varphi_B^*(2) d\tau_1 d\tau_2$$

In simple molecules bonding leads to singlet ground states

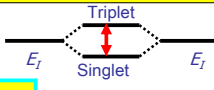
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Exchange Interaction and Bonding

$$E = 2E_i + \frac{C \pm A}{1 \pm S}$$

+ for singlet  
- for triplet



Size of splitting defined as exchange constant J  $E_t - E_s = 2 \frac{CS - A}{1 - S^2} \equiv -J$

Generalization to many atoms: Heisenberg Hamiltonian

$$H = \sum_i \sum_{j \neq i} 2J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

Ferromagnetic coupling for positive J  $\uparrow\uparrow$   
 Antiferromagnetic for negative J  $\uparrow\downarrow$

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