

Hyperfine Splitting

in ground state of Hydrogen

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Introduction

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- We then apply our mechanism to exotic atoms like - **positronium**, **muonium**, and **muonic hydrogen**.
- Finally, we have an intuitive discussion on **Why is the Singlet level lower?**

Origin of the Vector Potential Equation

Expression for $\mathbf{A}(\mathbf{r})$ originates from Maxwell's equations for magnetostatics. (Proof in appendix)

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The magnetic field $\mathbf{B}(\mathbf{r})$ is **curl** of the vector potential ($\mathbf{B} = \nabla \times \mathbf{A}$).

$$\nabla \times \mathbf{A}(\mathbf{r}) = \mathbf{B}(\mathbf{r}) = \left(\frac{\mu_0}{4\pi} \right) \left(\frac{1}{r^3} \right) [3(\mathbf{m} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{m}] \quad (3)$$

Theorem : Statement

Theorem : The average magnetic field over a spherical volume of radius R , due to an arbitrary configuration of steady currents within the sphere, is

$$\mathbf{B}_{\text{av}} = \left(\frac{\mu_0}{4\pi} \right) \frac{2\mathbf{m}}{R^3} \quad (4)$$

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where $\mathbf{m}$ is the total dipole moment of the sphere.

The Failure of the Standard Dipole Field

we derived the magnetic field

$$\mathbf{B}_{\text{out}}(\mathbf{r}) = \frac{\mu_0}{4\pi r^3} [3(\mathbf{m} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{m}] \quad (5)$$

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- Theorem states the average field over a sphere is $\mathbf{B}_{\text{av}} = \frac{\mu_0}{4\pi} \frac{2\mathbf{m}}{R^3}$.
- If we attempt to integrate $\mathbf{B}_{\text{out}}$ over a spherical volume to find the average, the integral is indeterminate due to the strong singularity at $r = 0$. So this model ignores what happens in the origin .

The Internal Field from a Boundary Value Problem

To resolve , we treat the ideal point dipole as the **limit of a uniformly magnetized sphere of radius a and magnetization $\mathbf{M}$** , where $\mathbf{m} = \frac{4}{3}\pi a^3 \mathbf{M}$.

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$$\mathbf{B}_{\text{in}}(\mathbf{r}) = \frac{2}{3}\mu_0 \mathbf{M} = \left(\frac{\mu_0}{2\pi}\right) \frac{\mathbf{m}}{a^3} \quad \text{for } r < a \quad (6)$$

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While the field outside ($r > a$) exactly matches our standard dipole field $\mathbf{B}_{\text{out}}$.

Motivating the Delta Function

Consider the ideal dipole limit where the sphere shrinks to a point ($a \rightarrow 0$):

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- The internal field magnitude goes to infinity ($\mathbf{B}_{\text{in}} \propto 1/a^3$).

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Crucially, the volume integral of this internal field remains constant, regardless of a :

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A function that is infinite at the origin, zero everywhere else, and has a finite integral is exactly the **Dirac delta function**.

$$\lim_{a \rightarrow 0} \mathbf{B}_{\text{in}}(\mathbf{r}) = \frac{2}{3}\mu_0 \mathbf{m} \delta^3(\mathbf{r}) \quad (8)$$

The Complete Magnetic Field

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The complete magnetic field of an ideal dipole is:

$$\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi r^3} [3(\mathbf{m} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{m}] + \frac{2}{3}\mu_0 \mathbf{m} \delta^3(\mathbf{r}) \quad (9)$$

The Hyperfine Hamiltonian

The Hyperfine Hamiltonian

We shall deduce the Hyperfine term in the Hydrogen Hamiltonian, due to the interaction of the magnetic dipole $\mathbf{m}_e$ (of the electron), with the dipolar magnetic field $\mathbf{B}_p$ (of the proton/nucleus).

$$H_{\text{HFS}} = -\mathbf{m}_e \cdot \mathbf{B}_p(\mathbf{r})$$

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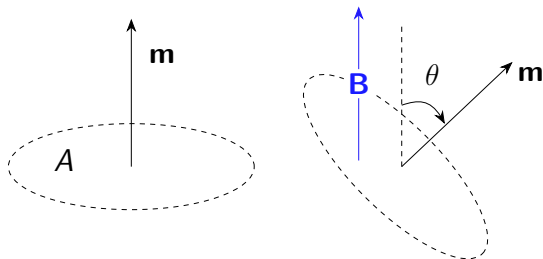
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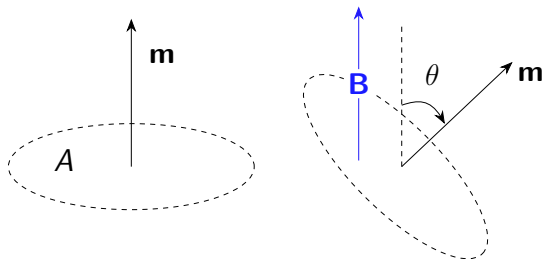
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- To derive this interaction energy, we first derive general potential energy of a magnetic dipole in an external magnetic field.

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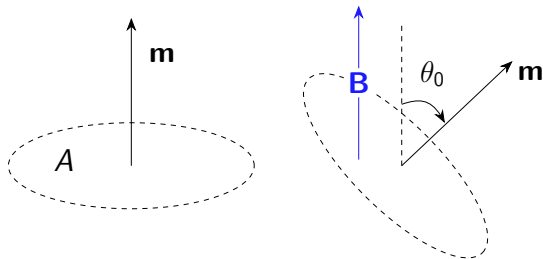
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In the presence of an external magnetic field $\mathbf{B}$, if our dipole makes an angle θ , at any time t , the magnitude of **torque** acting on it is,

$$\boldsymbol{\tau} = \mathbf{m} \times \mathbf{B} = mB \sin \theta \hat{k}$$

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- at an *infinitesimal* angular speed and **without angular acceleration**,

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$$U(\theta) = mB(\cos \pi/2 - \cos \theta) = -mB \cos \theta = -\mathbf{m} \cdot \mathbf{B}$$

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- Identifying interaction energy as the perturbation Hamiltonian:

$$H_{\text{HFS}} = -\mathbf{m}_e \cdot \mathbf{B}_p(\mathbf{r})$$

The Hyperfine Hamiltonian

$$\begin{aligned} H_{\text{HFS}} &= -\mathbf{m}_e \cdot \mathbf{B}_p(\mathbf{r}) \\ &= -\frac{\mu_0}{4\pi} \frac{3(\hat{\mathbf{r}} \cdot \mathbf{m}_e)(\hat{\mathbf{r}} \cdot \mathbf{m}_p) - \mathbf{m}_e \cdot \mathbf{m}_p}{r^3} - \frac{2\mu_0}{3} \mathbf{m}_e \cdot \mathbf{m}_p \delta(\mathbf{r}) \end{aligned}$$

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dipole-dipole interaction

contact interaction

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The H_{HFS} is then:

$$H_{\text{HFS}} = \gamma_e \gamma_p \left(-\frac{\mu_0}{4\pi} \frac{3(\hat{\mathbf{r}} \cdot \mathbf{S}_e)(\hat{\mathbf{r}} \cdot \mathbf{S}_p) - \mathbf{S}_e \cdot \mathbf{S}_p}{r^3} - \frac{2\mu_0}{3} \mathbf{S}_e \cdot \mathbf{S}_p \delta(\mathbf{r}) \right)$$

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Therefore, the complete Hamiltonian for the problem is:

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and, H_{HFS} is given as:

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Therefore, to solve the above problem, **Degenerate perturbation theory** must be invoked.

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where the chosen degenerate eigenstates $|n^{(0)}; k\rangle$ of $H^{(0)}$ are also the eigenstates of δH , also known as the **good basis states**

Application of DPT to HFS problem

For our problem, the unperturbed Hamiltonian $H^{(0)}$ is the Hydrogen atom Hamiltonian H_{atom}

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where $|k\rangle$ is some linear combination of the spin states¹

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Energy Correction

Therefore, the first order corrected energy is

$$E_{0,k}^{(1)} = \langle \psi_{100}; k | H_{\text{HFS}} | \psi_{100}; k \rangle$$

where, we recall that ψ_{100} is the **unperturbed ground state** s-orbital wavefunction.

$$\psi_{100}(r, \theta, \phi) = (\pi a^3)^{-1/2} e^{-r/a}$$

where $a = \hbar^2 / me^2 = 0.0529 \text{ nm}$ (First Bohr Radius)

Energy Correction

Therefore,

$$\Delta E_{0,k}^{(1)} = \langle \psi_{100}; k | H_{\text{HFS}} | \psi_{100}; k \rangle$$

$$\langle \mathbf{r} | \psi_{100}; k \rangle = \psi_{100}(r, \theta, \phi) |k\rangle = (\pi a^3)^{-1/2} e^{-r/a} |k\rangle$$

Excluding constants,

$$\begin{aligned} \therefore E_{0,k}^{(1)} \sim \langle k | & \left(\int_{\mathbb{R}^3} d\Omega dr r^2 \frac{3(\hat{\mathbf{r}} \cdot \mathbf{m}_e)(\hat{\mathbf{r}} \cdot \mathbf{m}_p) - \mathbf{m}_e \cdot \mathbf{m}_p}{r^3} e^{-2r/a} \right. \\ & \left. - \int_{\mathbb{R}^3} r^2 dr d\Omega (\mathbf{m}_e \cdot \mathbf{m}_p) |\psi_{100}(\mathbf{r})|^2 \delta(\mathbf{r}) \right) |k\rangle \end{aligned}$$

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$\uparrow$
 $= \sin \theta d\theta d\phi$

Theorem

Let $\mathbf{a}$ and $\mathbf{b}$ be two constant vectors.

$$\int_\Omega (\mathbf{a} \cdot \hat{\mathbf{r}})(\mathbf{b} \cdot \hat{\mathbf{r}}) d\Omega = \frac{4\pi}{3} (\mathbf{a} \cdot \mathbf{b})$$

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So, second term reduces to

$$-\frac{2\mu_0}{3\pi a^3} \langle \mathbf{m}_e \cdot \mathbf{m}_p \rangle$$

Energy Correction

Substitute,

$$\mathbf{m}_e = -g_e \frac{e}{2m_e} \mathbf{S}_e ; \mathbf{m}_p = g_p \frac{e}{2m_p} \mathbf{S}_p$$

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This gives,

$$E_{0;k}^{(1)} = \frac{\mu_0 g_e g_p e^2}{6\pi m_e m_p a^3} \langle \mathbf{S}_e \cdot \mathbf{S}_p \rangle$$

for the ground state. It is also known as **spin-spin coupling**.

Conserved Quantity

The effective perturbation Hamiltonian is thus reduced to the **spin-spin coupling** term. In its presence, the z-component of the $\mathbf{S}_e$ and $\mathbf{S}_p$ are not conserved quantities anymore and hence are not “good” quantum numbers.

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This can be further seen as follows:

$$[\mathbf{S}_e \cdot \mathbf{S}_p, S_p^{(z)}] = i\hbar \left(S_e^{(y)} S_p^{(x)} - S_e^{(x)} S_p^{(y)} \right) \neq 0$$

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One can easily check that $F^{(z)}$ and F^2 are conserved quantities for the problem.

$$[\mathbf{S}_e \cdot \mathbf{S}_p, F^{(z)}] = 0$$

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Good Basis States

The good basis states are then the common eigenstates of $F^{(z)}$ and F^2 operator and hence the choice for our $|k\rangle$ states

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Triplet States ($f = 1$):

$$|1, 1\rangle = |\uparrow_e \uparrow_p\rangle$$

$$|1, 0\rangle = \frac{1}{\sqrt{2}} (|\uparrow_e \downarrow_p\rangle + |\downarrow_e \uparrow_p\rangle)$$

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Energy Correction

The final energy correction is thus:

$$E_0^{(1)} = \frac{\mu_0 g_e g_p e^2 \hbar^2}{6\pi m_e m_p a^3} \begin{cases} \frac{1}{4} & \text{(Triplet)} \\ -\frac{3}{4} & \text{(Singlet)} \end{cases}$$

Energy Correction

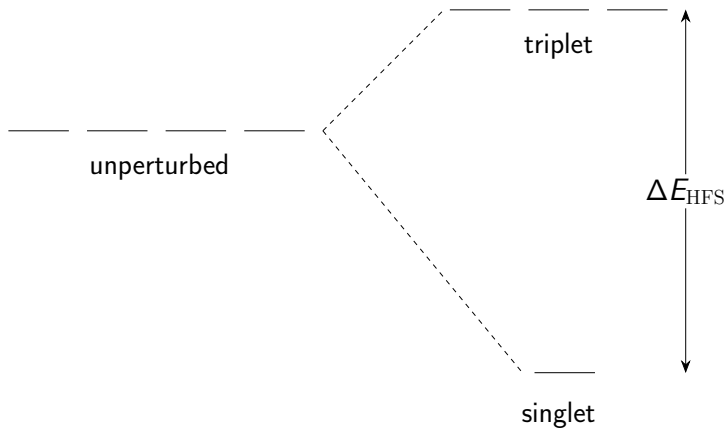
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The **energy gap** between the triplet and singlet states is given as:

$$\Delta E_{\text{HFS}} = \frac{\mu_0 g_e g_p e^2 \hbar^2}{6\pi m_e m_p a^3}$$

Lifting of Degeneracy



Calculation for H-Atom

HFS splitting: Normal Hydrogen

We substitute the values: $g_e = 2.0023$ $g_p = 5.5857$

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The discrepancy of approx. **2.4 MHz** can be explained through Quantum Electrodynamics corrections

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The **fine structure** on the other hand goes like $\frac{R^2}{m_e c^2}$, and is therefore typically greater by a factor on the order of $\frac{m_p}{m_e} = 1836$

Calculations for Exotic Atoms

HFS Splitting: Positronium

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Applying the reduced mass correction, one obtains:

$$\Delta E_{\text{HFS,pos}} = \frac{1}{8} \left(1 + \frac{m_e}{m_p} \right)^3 \left(\frac{g_e}{g_p} \right) \left(\frac{m_p}{m_e} \right) \times \Delta E_{\text{HFS,hyd}} = 4.849 \times 10^{-4} \text{ eV}$$

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The discrepancy with the experimental value of $8.411 \times 10^{-4} \text{ eV}$ is primarily due to **pair annihilation**, which adds an additional $\frac{3}{4} \Delta E_{\text{HFS, pos}}$ to the splitting.

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This matches well with the experimental value of $1.8458885 \times 10^{-5} \text{ eV}$.
The **0.2%** discrepancy is a result of quantum electrodynamical corrections.

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This corresponds to a wavelength of **67800 Å**, in the infrared region. Note that, this quantity has not yet been measured directly in the laboratory.

Discussions

Full Expression of Interaction Energy

Electric Dipole-Dipole Interaction Energy (W_E):

$$W_E = \frac{1}{4\pi\epsilon_0} \left[\frac{\mathbf{p}_1 \cdot \mathbf{p}_2 - 3(\mathbf{p}_1 \cdot \hat{\mathbf{r}})(\mathbf{p}_2 \cdot \hat{\mathbf{r}})}{r^3} + \frac{4\pi}{3} (\mathbf{p}_1 \cdot \mathbf{p}_2) \delta^3(\mathbf{r}) \right] \quad (10)$$

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Magnetic Dipole-Dipole Interaction Energy (W_M):

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Claim: At large distances ($r \gg$ dipole size), only $1/r^3$ is in the interaction.

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Alignment: The minimum energy occurs at $\theta_1 = \theta_2 = 0$. Or $\theta_1 = \theta_2 = \pi$

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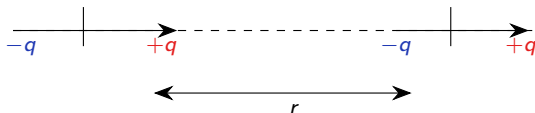


Figure: Electric Dipoles ($r \rightarrow \infty$)

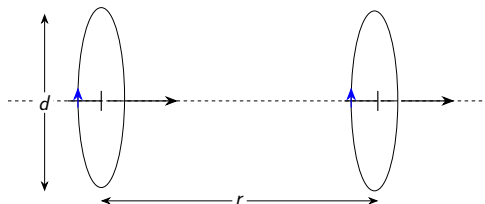


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- **Magnetic Dipoles:** Modeled as circular current loops. Parallel currents attract. As they merge at $r \rightarrow 0$, the currents flow in the same direction, forcing them to lie **parallel**.

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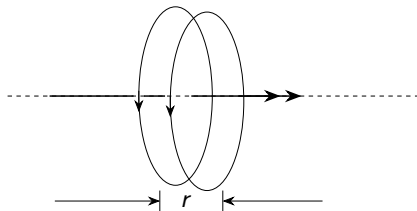


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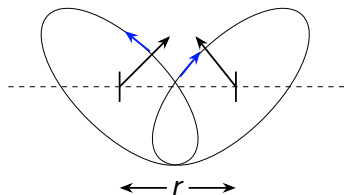


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Singlet vs. Triplet States in Hydrogen

In the ground state of hydrogen, the electron and proton wavefunctions overlap, meaning $r = 0$ is highly probable. The delta-function term dictates the energy splitting.

The States:

- **Singlet State:** Proton and electron spins are *antiparallel*. Because of their intrinsic properties, this means their **magnetic moments are parallel**.
- **Triplet State:** Proton and electron spins are *parallel*, meaning their magnetic moments are *antiparallel*.

Energy Claim: Because the magnetic delta-function interaction strongly favors **parallel** magnetic moments as $r \rightarrow 0$, the **singlet state** minimizes the interaction energy. Therefore, the singlet state represents the lowest energy configuration (ground state hyperfine splitting).

THANK YOU SIR :)

References I



Griffiths, D. J. (1982).

Hyperfine splitting in the ground state of hydrogen.

American Journal of Physics, 50(8):698–703.

Applications

Astrophysical Applications: The 21 cm Line

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- **Cosmology:** It is the primary tool for observing the universe's *Dark Ages* — the era before any star formation.

Broader Spectroscopic & Technological Applications

Key Technologies:

- **Atomic Clocks (Metrology):**

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- **Electron Spin Resonance (ESR):**

Magnetic dipole transitions of unpaired electrons. It is heavily utilized in biochemistry and materials science to study free radicals and defect centers.