

Spring 1-1-2001

Hyperfine Interaction in the Hydrogen Atom

Ronald Lovett

Washington University in St. Louis

Follow this and additional works at: https://openscholarship.wustl.edu/chem_papers



Part of the [Chemistry Commons](#)

Recommended Citation

Lovett, Ronald, "Hyperfine Interaction in the Hydrogen Atom" (2001). *Topics in Quantum Mechanics*. 10.
https://openscholarship.wustl.edu/chem_papers/10

This Classroom Handout is brought to you for free and open access by the Chemistry at Washington University Open Scholarship. It has been accepted for inclusion in Topics in Quantum Mechanics by an authorized administrator of Washington University Open Scholarship. For more information, please contact digital@wumail.wustl.edu.

Hyperfine interactions in the Hydrogen atom

The H atom's Hamiltonian

Let \mathbf{r}_e locate the electron and \mathbf{r}_p locate the proton in the H atom. If m (M) is the mass of the electron (proton), the contributions of the kinetic energy to the H -atom's Hamiltonian are

$$\hat{H}_0 = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_e^2} - \frac{\hbar^2}{2M} \frac{\partial^2}{\partial \mathbf{r}_p^2} \quad (1)$$

If

$$\begin{aligned} \mathbf{r} &= \mathbf{r}_e - \mathbf{r}_p, \\ \mathbf{R} &= \frac{M \mathbf{r}_p + m \mathbf{r}_e}{M + m}, \end{aligned}$$

\mathbf{R} locates the center of mass of the atom while \mathbf{r} gives the position of the electron relative to that of the proton.

The coordinate transformation: $\mathbf{r}_e, \mathbf{r}_p \rightarrow \mathbf{r}, \mathbf{R}$ maps \hat{H}_0 into

$$\hat{H}_0 = \left[-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial \mathbf{R}^2} \right] + \left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \mathbf{r}^2} \right]. \quad (2)$$

\hat{H}_0 is separable into a center of mass contribution and an internal contribution. We will focus on the internal contribution, adding the Coulombic interaction between the electron and proton to the second term in (2) to get

$$\hat{H}_1 = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \mathbf{r}^2} - \frac{e^2}{4\pi\epsilon_0 r} \quad (3)$$

The ground state wave function associated with \hat{H}_1 is

$$\psi_{1S}(r) = \frac{e^{-r/a}}{\sqrt{\pi a^3}} \quad (4)$$

with

$$a = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2}$$

The μ is very close to the electronic mass m and a is very close to the Bohr radius

$$a_0 = 0.52918 \text{ \AA}$$

The angular momentum

The description in (3) is incomplete: The electron and the proton in hydrogen are spin- $\frac{1}{2}$ particles. In the ground state (4) all the angular momentum of the atom is associated with these spins. Thus there are two spin angular momentum operators, the spin of the electron \hat{S}_e and the spin of the proton \hat{S}_p . Because of the rotational invariance of the hydrogen atom, \hat{H}_1 commutes with the total angular momentum,

$$\hat{S} = \hat{S}_e + \hat{S}_p,$$

and we can construct states that are simultaneously eigenfunctions of \hat{H}_1 , \hat{S}_z and \hat{S}^2 .

Since each spin can be represented in terms of an α, β basis set, the atom's spin state can be represented in the basis set

$$\psi_{\uparrow\uparrow} = \alpha_e\alpha_p, \quad \psi_{\uparrow\downarrow} = \alpha_e\beta_p, \quad \psi_{\downarrow\uparrow} = \beta_e\alpha_p, \quad \psi_{\downarrow\downarrow} = \beta_e\beta_p. \quad (5)$$

While S_z is diagonal in the basis set (5), S^2 is not.

Magnetic interaction

The electron and protons have a magnetic moment. It has the same orientation as the intrinsic spins of these particles and is hence characterized by giving a *gyromagnetic ratio* γ_e (< 0) and γ_p so that

$$\begin{aligned} \mu_e &= \gamma_e \hat{S}_e \\ \mu_p &= \gamma_p \hat{S}_p \end{aligned}$$

The interaction between the two magnetic moments (a typical dipole-dipole interaction) contributes a term

$$\begin{aligned} V(\mathbf{r}) &= -\frac{\mu_0}{4\pi} \frac{3(\mu_e \cdot \mathbf{r})(\mu_p \cdot \mathbf{r}) - r^2 \mu_e \cdot \mu_p}{r^5} \\ &= -\frac{\mu_0 \gamma_e \gamma_p}{4\pi} \frac{3(\hat{S}_e \cdot \mathbf{r})(\hat{S}_p \cdot \mathbf{r}) - r^2 \hat{S}_e \cdot \hat{S}_p}{r^5} \end{aligned} \quad (6)$$

to the Hamiltonian of the system.†

† *N.B.:* The μ_0 in (6) is one of the *SI* constants used in *EM* courses.

The orbital average

In the ground state, the expected value of the contribution of the magnetic interactions to the energy of the atom will be

$$\Delta E = \int dr V(r) |\psi_{1S}(r)|^2 = \frac{\mu_0 \gamma_e \gamma_p \hbar^2}{\pi a^3} \hat{S}_e \cdot \hat{S}_p \quad (7)$$

Evaluation of this integral is tricky. Details are presented in the Appendix.

The term in (7) is diagonal in the basis set that diagonalizes \hat{S}^2 and \hat{S}_z^2 . The interaction (7) splits the ground $1S$ state of the hydrogen atom into two levels.

Spectroscopic Observation

The first calculation of ΔE was made (in 1944) by a graduate student at Leiden University, H. C. Van de Hulst. The frequency of the radiation associated with this transition is $\sim 1420.405 MHz$ (the wavelength is $\sim 21cm$). Radiation at this frequency from interstellar matter was reported simultaneously in the Netherlands, in the U.S., and in Australia in 1951.

Appendix

Consider the evaluation of the integral

$$I_{ij} = \int dv \frac{3x_i x_j - r^2 \delta_{ij}}{r^5} f(r) \quad (\text{A1})$$

The integral in (7) can be recovered by proper choice of $f(r)$ and *contraction* with the spin operators

$$\hat{S}_{e,i} I_{ij} \hat{S}_{p,j}$$

The evaluation of this integral is tricky if $f(r)$ is spherically symmetric, for if the integration is performed on spherical shells, the integral over a shell of radius r gives

$$\langle x_i x_j \rangle = \frac{1}{3} r^2 \delta_{ij}$$

and hence makes no contribution to I_{ij} . A non-zero result is only possible because of the singularity in the integrand of (A1) at $r = 0$.

If we expand $f(r)$ in r about $r = 0$, the argument about the spherical averages leading to zero says

$$I_{ij} = f(0) \int dv \frac{3x_i x_j - r^2 \delta_{ij}}{r^5} \quad (\text{A2})$$

If $i \neq j$, the integrand in (A2) will be odd in each of two directions and so the integral will be zero. Thus a non-zero result can only arise when $i = j$. Since all $i = j$ values give the same result,

$$I_{ij} = \frac{1}{3} I \delta_{ij} f(0) \quad (\text{A3})$$

with I the sum of the I_{ii} values over $i = 1, 2, 3$.

Now

$$\int dv \left(\frac{3x_i x_j}{r^5} - \frac{\delta_{ij}}{r^3} \right) = \int dv \frac{\partial^2}{\partial x_i \partial x_j} \left(\frac{1}{r} \right)$$

so the I in (A3) is just

$$I = f(0) \int dv \nabla^2 \frac{1}{r}.$$

Again,

$$\nabla^2 \frac{1}{r}$$

has an orientational average of zero at all $r > 0$ but is singular at $r = 0$. Since

$$\int_{r < R} dv \nabla^2 \frac{1}{r} = - \int_{r < R} dv \nabla \cdot \frac{\mathbf{r}}{r^3} = - \int_{r=R} d\mathbf{S} \cdot \frac{\mathbf{r}}{r^3} = -4\pi,$$

we identify

$$\begin{aligned}\nabla^2 \frac{1}{r} &= -4\pi \delta(\mathbf{r}), \\ I &= -4\pi f(0), \\ I_{ij} &= -\frac{4\pi}{3} f(0) \delta_{ij}.\end{aligned}$$

Thus

$$\hat{S}_{e,i} I_{ij} \hat{S}_{p,j} = -\frac{4\pi}{3} f(0) \hat{S}_e \cdot \hat{S}_p$$

A coupling of two vectors of the form $\vec{A} \cdot \vec{B}$ is often referred to as a *scalar* coupling. As it was E. Fermi who first recognized that I_{ij} would have a non-zero value associated with the probability of finding the two magnetic moments on top of each other, the term is usually referred to as the *Fermi contact term*.

Problem Set #8

Show that the expression in (2) follows from that in (1) and identify what the constants μ and \mathcal{M} are.

2. Show that the Hamiltonian in (2) is separable. Describe the two separated problems in simple physical terms.
3. Explain what the terms in H_1 (Eqn.(3)) represent.
4. Determining the results of applying \hat{S}^2 to the basis vectors in (5) is facilitated by recalling that

$$\begin{aligned}\hat{S}^2 &= \hat{S}_+ \hat{S}_- + \hat{S}_z^2 - \hbar \hat{S}_z \\ &= \hat{S}_- \hat{S}_+ + \hat{S}_z^2 + \hbar \hat{S}_z\end{aligned}$$

Show that the basis vectors in (5) do not diagonalize \hat{S}^2 . In what basis set are both S_z and S^2 diagonal? Characterize this basis set physically.

5. Show that

$$\hat{\mathbf{S}}_e \cdot \hat{\mathbf{S}}_p = \frac{1}{2} (\hat{S}^2 - \hat{S}_e^2 - \hat{S}_p^2)$$

and use this to show that the basis vectors that diagonalize S_z and S^2 also diagonalize the energy in (7).

6. Show that the splitting of the $1S$ level is

$$\Delta E = \frac{2\mu_0\gamma_e\gamma_p\hbar^2}{\pi a^3}$$