## 221A Lecture Notes

## Fine and Hyperfine Structures of the Hydrogen Atom

## 1 Introduction

With the usual Hamiltonian for the hydrogen-like atom (in the Gaussian unit),

$$
\begin{equation*}
H_{0}=\frac{\vec{p}^{2}}{2 m}-\frac{Z e^{2}}{r}, \tag{1}
\end{equation*}
$$

we have the $n^{2}$-fold degeneracy of states with the same principal quantum number, or $2 n^{2}$-fold once the spin degrees of freedom is included. In the real world, however, the degeneracy is lifted by corrections that arise due to the special relativity. Note also that $m$ in the Hamiltonian is not the mass of the electron, but the reduced mass $m=\left(m_{e} m_{p}\right) /\left(m_{e}+m_{p}\right)$ which is smaller than the electron mass by about $0.05 \%$.

It is useful to recall that the electron in the hydrogen atom is nonrelativistic, $v \ll c$, but not that slow. The expectation value of the kinetic energy for the state $|n l m\rangle$ is

$$
\begin{equation*}
\langle n l m| \frac{\vec{p}^{2}}{2 m}|n l m\rangle=\frac{Z e^{2}}{2 a_{0}}=\frac{\left(Z e^{2}\right)^{2} m}{2 \hbar^{2}}=\frac{1}{2} Z^{2} \alpha^{2}\left(m c^{2}\right) . \tag{2}
\end{equation*}
$$

Equating it with $\frac{1}{2} m v^{2}$, we find $v=Z \alpha c$, and even for $Z=1$ the electron is moving at about $1 \%$ of the speed of light. We expect relativistic effects arise suppressed by $(v / c)^{2}=(Z \alpha)^{2}$ to the usual energy levels, namely $(Z \alpha)^{4} m c^{2}$ approximately.

Another interesting point is that the deuterium ${ }^{2} \mathrm{H}$, whose nucleus deuteron is a bound state of a proton and nucleon, has a slightly different energy spectrum. Its reduced mass $m=\left(m_{e} m_{d}\right) /\left(m_{e}+m_{d}\right)$ is about $0.025 \%$ different, and hence the entire energy spectrum is scaled by the same amount. Even though the difference sounds tiny, it is well detectable in spectroscopy. In fact, the abundance of deuterium in the universe had been determined by the slight shifts in the absorption lines where a hydrogen gas is "back-lit" by distant quasars. See, e.g., David tytler, Xiao-Ming Fan, and Scott Burles, Nature, 381, 207-209 (2002); or http://www. spacedaily.com/news/cosmology-01c . html. The deuterium abundance provides one of the best ways to test the

Big-Bang cosmology by comparing the calculation of light element abundances to the observation. See, e.g., http://astron.berkeley.edu/~mwhite/ darkmatter/bbn.html by our own Martin White.

## 2 Fine Structure

The fine structure of the hydrogen atom refers to the $(Z \alpha)^{2}$ correction to the energy levels. It consists of three perturbation Hamiltonians. The first one is the relativistic correction

$$
\begin{equation*}
H_{r c}=-\frac{\left(\vec{p}^{2}\right)^{2}}{8 m^{3} c^{2}} \tag{3}
\end{equation*}
$$

which arises from the expansion of the relativistic kinetic energy

$$
\begin{equation*}
\sqrt{m^{2} c^{4}+\vec{p}^{2} c^{2}}=m c^{2}+\frac{\vec{p}^{2}}{2 m}-\frac{\left(\vec{p}^{2}\right)^{2}}{8 m^{3} c^{2}}+O\left(p^{6}\right) \tag{4}
\end{equation*}
$$

The next one is the spin-orbit coupling

$$
\begin{equation*}
H_{L S}=+g \frac{1}{4 m_{e}^{2} c^{2}} \frac{1}{r} \frac{d V_{c}}{d r}(\vec{L} \cdot \vec{S}) \tag{5}
\end{equation*}
$$

Of course the central potential is $V_{c}=Z e^{2} / r$ for the hydrogen atom, but it is left general so that it is applicable to multi-electron atoms as we will discuss in 221B. The Coulomb field of the proton (or nucleus) appears partially as a magnetic field in the moving reference frame of the electron, and the magnetic moment of the electron $\vec{\mu}=\frac{e}{2 m c}(\vec{L}+g \vec{S})$. However, this argument suggests twice as large contribution, as discussed in Sakurai, p. 305.

When Goudsmit and Uhlenbeck suggested the electron spin, apparently Heisenberg wrote to them immediately asking what they have done with a factor of two. They didn't think they could calculate the spin-orbit correction, and they hadn't. If they had, they may not have had courage to publish it, according to Goudsmit's reminiscence at http://www.lorentz. leidenuniv.nl/history/spin/goudsmit.html. L.H. Thomas, in his paper Nature 107, 514 (1926), pointed out that this naive calculation is incorrect. Because is the electron goes around the nucleus, and namely has a constant acceleration, the native Lorentz transformation of the electric field to the magnetic field does not give the right answer. One has to set up the reference frame that is always parallel to each other, which inevitably rotates
around in the electron rest frame. "The Story of Spin" by Sin-itiro Tomonaga has a detailed account on this point. At the end of the day, Thomas showed that the spin-orbit coupling is a factor of two smaller than the naive expectation, leading to the above Hamiltonian.

The third and the last one is the so-called Darwin term,

$$
\begin{equation*}
H_{\text {Darwin }}=\frac{\hbar^{2}}{8 m_{e}^{2} c^{2}} \Delta V_{c} . \tag{6}
\end{equation*}
$$

$\Delta=(\vec{\nabla})^{2}$ is the Laplacian. Note that, for the Coulomb potential $V_{c}=$ $-Z e^{2} / r$, it becomes a delta function

$$
\begin{equation*}
H_{\text {Darwin }}=\frac{\hbar^{2}}{8 m_{e}^{2} c^{2}} 4 \pi Z e^{2} \delta(\vec{x}) \tag{7}
\end{equation*}
$$

because $\Delta \frac{1}{r}=-4 \pi \delta(\vec{r})$. The origin of this term is more subtle than the previous two terms.

The relativistic wave equation was written down by Dirac, which we will discuss in 221 B . It predicted the existence of anti-matter, namely positron for the electron and anti-proton for the proton, which were discovered later by Caltech group (positron) and Berkeley group (anti-proton). At the same time, it was a fully relativistic theory that predicts both the relativistic correction and the spin-orbit coupling automatically without resorting to any arguments. They just come out from the equation. In addition, the wave equation predicts that the relativistic electron doesn't sit quietly. It undergoes a frantic back-and-forth motion which Schrödinger named Zitterbewegung, a German word made of "jitter" and "motion." The position of the electron is "smeared" due to this motion by a distance of so-called the Compton wavelength $\hbar / m_{e} c \simeq 4 \times 10^{-11} \mathrm{~cm}$. Therefore the potential energy the electron experiences is not strictly at a particular position, but rather an "average" around that point. The correction can be computed in a Taylor expansion around the average position $r_{0}$,

$$
\begin{equation*}
V_{c}(r)=V_{c}\left(r_{0}\right)+\langle(\Delta \vec{r})\rangle \cdot \vec{\nabla} V_{c}\left(r_{0}\right)+\frac{1}{2!}\left\langle\left(\Delta r^{i}\right)\left(\Delta r^{j}\right)\right\rangle \vec{\nabla}_{i} \vec{\nabla}_{j} V_{c}\left(r_{0}\right), \tag{8}
\end{equation*}
$$

and the spherical symmetry of Zitterbewegung says $\left\langle\Delta r^{i}\right\rangle=0$, and $\left\langle\left(\Delta r^{i}\right)\left(\Delta r^{j}\right)\right\rangle=$ $\left(\frac{\hbar^{2}}{4 m_{e}^{2} c^{2}}\right)^{2} \delta^{i j}$. This argument leads to the Darwin term above. Again, the Dirac theory leads to this term automatically as we will see in 221B.

The first-order energy shifts due to these perturbations are simply expectation values with respect to the unperturbed states. The only tricky aspect is that the unperturbed states are degenerate. However, it is easy to see that the spin-orbit coupling is diagonal in the eigenstates of the total angular momentum $\vec{J}^{2}\left|n j l m_{j}\right\rangle=j(j+1) \hbar^{2}\left|n j l m_{j}\right\rangle$ and $J_{z}\left|n j l m_{j}\right\rangle=\hbar m_{j}\left|n j l m_{j}\right\rangle$, and this is the basis we use.

First with the relativistic correction. Using the unperturbed Hamiltonian,

$$
\begin{equation*}
\frac{\vec{p}^{2}}{2 m}\left|n j l m_{j}\right\rangle=\left(-\frac{Z e^{2}}{2 n^{2} a}+\frac{Z e^{2}}{r}\right)\left|n j l m_{j}\right\rangle, \tag{9}
\end{equation*}
$$

we can rewrite

$$
\begin{align*}
& \left\langle n j l m_{j}\right| H_{r c}\left|n j l m_{j}\right\rangle=-\frac{1}{2 m c^{2}}\left\langle n j l m_{j}\right|\left(-\frac{Z e^{2}}{2 n^{2} a}+\frac{Z e^{2}}{r}\right)^{2}\left|n j l m_{j}\right\rangle \\
& \quad=-\frac{\left(Z e^{2}\right)^{2}}{2 m c^{2}}\left(\frac{1}{4 n^{4} a^{2}}-\frac{1}{n^{2} a}\left\langle\frac{1}{r}\right\rangle+\left\langle\frac{1}{r^{2}}\right\rangle\right) \\
& =-\frac{\left(Z e^{2}\right)^{2}}{2 m c^{2}}\left(\frac{1}{4 n^{4} a^{2}}-\frac{1}{n^{2} a} \frac{1}{n^{2} a}+\frac{1}{n^{3} a^{2}\left(l+\frac{1}{2}\right)}\right) \\
& =-\frac{\left(Z e^{2}\right)^{2}}{2 m c^{2}} \frac{1}{4 n^{4} a^{2}}\left(\frac{4 n}{l+\frac{1}{2}}-3\right) \\
& =-\frac{(Z \alpha)^{4} m c^{2}}{8 n^{4}}\left(\frac{4 n}{l+\frac{1}{2}}-3\right) \\
& =-\frac{(Z \alpha)^{4} m c^{2}}{8 n^{4}} \times \begin{cases}\left(\frac{4 n}{j}-3\right) & \left(j=l+\frac{1}{2}\right) \\
\left(\frac{4 n}{j+1}-3\right) & \left(j=l-\frac{1}{2}\right)\end{cases} \tag{10}
\end{align*}
$$

Here, I used the formulae in Eq. (A.6.8) in Sakurai with $a=a_{0} / Z=$ $\hbar^{2} /\left(Z e^{2} m\right)=\hbar c /\left(Z \alpha m c^{2}\right)$.

For the spin-orbit coupling, we use the identity

$$
\begin{align*}
(\vec{L} \cdot \vec{S})\left|n j l m_{j}\right\rangle & =\frac{1}{2}\left(\vec{J}^{2}-\vec{L}^{2}-\vec{S}^{2}\right)\left|n j l m_{j}\right\rangle \\
& =\frac{\hbar^{2}}{2}\left(j(j+1)-l(l+1)-\frac{3}{4}\right)\left|n j l m_{j}\right\rangle \\
& =\frac{\hbar^{2}}{2} \times \begin{cases}\left(j-\frac{1}{2}\right)\left|n j l m_{j}\right\rangle & \left(j=l+\frac{1}{2}\right) \\
\left(-j-\frac{3}{2}\right)\left|n j l m_{j}\right\rangle & \left(j=l-\frac{1}{2}\right)\end{cases} \tag{11}
\end{align*}
$$

Using $V_{c}=-\frac{Z e^{2}}{r}$ and $g=2$,

$$
\begin{equation*}
H_{L S}=\frac{1}{2 m_{e}^{2} c^{2}} \frac{Z e^{2}}{r^{3}}(\vec{L} \cdot \vec{S}) \tag{12}
\end{equation*}
$$

and hence

$$
\left\langle n j l m_{j}\right| H_{L S}\left|n j l m_{j}\right\rangle=\frac{Z e^{2}}{2 m_{e}^{2} c^{2}} \frac{\hbar^{2}}{2}\left\langle\frac{1}{r^{3}}\right\rangle \times \begin{cases}\left(j-\frac{1}{2}\right) & \left(j=l+\frac{1}{2}\right)  \tag{13}\\ \left(-j-\frac{3}{2}\right) & \left(j=l-\frac{1}{2}\right)\end{cases}
$$

It is known that

$$
\begin{equation*}
\left\langle\frac{1}{r^{3}}\right\rangle=\frac{1}{a^{3}} \frac{1}{n^{3} l\left(l+\frac{1}{2}\right)(l+1)} \tag{14}
\end{equation*}
$$

(see, e.g., http://hep.ucsd.edu/~branson/130/130b/130b_notes_prod/node96. html). Note that this expectation value is singular for $l=0$, while $H_{L S}=0$ identically because $\vec{L}=0$ and it is not a problem. We obtain

$$
\begin{align*}
\left\langle H_{L S}\right\rangle & =\frac{Z e^{2}}{2 m_{e}^{2} c^{2}} \frac{\hbar^{2}}{2 n^{3} a^{3}} \times \begin{cases}\frac{1}{j\left(j+\frac{1}{2}\right)} & \left(j=l+\frac{1}{2}\right) \\
\frac{-1}{\left(j+\frac{1}{2}\right)(j+1)} & \left(j=l-\frac{1}{2}\right)\end{cases} \\
& =\frac{(Z \alpha)^{4} m c^{2}}{4} \frac{1}{n^{3}} \times \begin{cases}\frac{1}{j\left(j+\frac{1}{2}\right)} & \left(j=l+\frac{1}{2}\right) \\
\frac{1}{\left(j+\frac{1}{2}\right)(j+1)} & \left(j=\frac{1}{2}\right)\end{cases} \tag{15}
\end{align*}
$$

The Darwin term has an expectation value only for the $s$-states, because $\psi(r) \propto r^{l}$.

$$
\begin{equation*}
\left\langle H_{\text {Darwin }}\right\rangle=\frac{\hbar^{2}}{8 m_{e}^{2} c^{2}} 4 \pi Z e^{2}|\psi(0)|^{2}, \tag{16}
\end{equation*}
$$

Using (A.6.3) in Sakurai,

$$
\begin{equation*}
R_{n 0}(r)=-\left\{\left(\frac{2}{n a}\right)^{3} \frac{(n-1)!}{2 n[n!]^{3}}\right\}^{1 / 2} e^{-\rho / 2} L_{n}^{1}(\rho) \tag{17}
\end{equation*}
$$

with $\rho=2 r / n a$. Because $L_{n}^{1}(\rho)=\frac{d}{d \rho} L_{n}(\rho)$, we need $O(\rho)$ term in $L_{n}(\rho)$ to find $L_{n}^{1}(0)$. From Eq. (A.6.5),

$$
\begin{equation*}
L_{p}(\rho)=p!-p!p \rho+O\left(\rho^{2}\right) \tag{18}
\end{equation*}
$$

and hence

$$
\begin{equation*}
L_{p}^{1}(\rho)=-p!p+O(\rho) \tag{19}
\end{equation*}
$$

Therefore, $L_{p}^{1}(0)=-p!p$. We obtain

$$
\begin{equation*}
\psi(0)=R_{n 0}(0) Y_{0}^{0}=-\left\{\left(\frac{2}{n a}\right)^{3} \frac{(n-1)!}{2 n[n!]^{3}}\right\}^{1 / 2}(-n!n) \frac{1}{4 \pi}, \tag{20}
\end{equation*}
$$

and hence

$$
\begin{equation*}
|\psi(0)|^{2}=\left(\frac{2}{n a}\right)^{3} \frac{(n-1)!}{2 n[n!]^{3}}(n!n)^{2} \frac{1}{4 \pi}=\frac{1}{4 \pi} \frac{4}{n^{3}} . \tag{21}
\end{equation*}
$$

The expectation value then is

$$
\begin{equation*}
\left\langle H_{\text {Darwin }}\right\rangle=\frac{\hbar^{2}}{8 m_{e}^{2} c^{2}} 4 \pi Z e^{2} \frac{1}{4 \pi} \frac{4}{n^{3}}=\frac{(Z \alpha)^{2} m c^{2}}{2 n^{3}} \tag{22}
\end{equation*}
$$

Due to some reason, this expression coincides with that of the spin-orbit coupling when $l=0, j=1 / 2$.

Finally, we put them together:

$$
\begin{align*}
& \left\langle H_{r c}+H_{L S}+H_{\text {Darwin }}\right\rangle \\
& \quad=\frac{(Z \alpha)^{4} m c^{2}}{8 n^{3}} \times \begin{cases}-\frac{4}{j}+\frac{3}{n}+\frac{2}{j\left(j+\frac{1}{2}\right)} & \left(j=l+\frac{1}{2}\right) \\
-\frac{4}{j+1}+\frac{3}{n}-\frac{1}{\left(j+\frac{1}{2}\right)(j+1)} & \left(j=l-\frac{1}{2}\right)\end{cases} \\
& \quad=\frac{(Z \alpha)^{4} m c^{2}}{8 n^{4}} \times\left(3-\frac{8 n}{2 j+1}\right) . \tag{23}
\end{align*}
$$

It somehow depends only on $j$, no matter $j=l \pm \frac{1}{2}$. This is an accidental degeneracy between $2 s_{1 / 2}$ and $2 p_{1 / 2}$, between $3 s_{1 / 2}$ and $3 p_{1 / 2}$, between $3 p_{3 / 2}$ and $3 d_{3 / 2}$, etc.

As we will discuss in 221B, the Dirac equation predicts ${ }^{1}$

$$
\begin{equation*}
E_{n, j}=m c^{2}\left\{1+\left(\frac{Z \alpha}{n-j-\frac{1}{2}+\sqrt{\left(j+\frac{1}{2}\right)^{2}-(Z \alpha)^{2}}}\right)^{2}\right\}^{-1 / 2} \tag{24}
\end{equation*}
$$

and once expanded up to $O(Z \alpha)^{4}$, we find

$$
\begin{equation*}
E_{n, j}=m c^{2}-\frac{(Z \alpha)^{2}}{2 n^{2}}+\frac{(Z \alpha)^{4}(6 j+3-8 n)}{8(2 j+1) n^{4}}+O(Z \alpha)^{6} \tag{25}
\end{equation*}
$$

[^0]which agrees with Eq. (23).
The degeneracy between $2 s_{1 / 2}$ and $2 p_{1 / 2}$ etc is actually lifted by the Lamb shift. This is an effect understood only in the QED (Quantum ElectroDynamics) which takes the zero-point fluctuation of photons as well as the polarization of the "vacuum" filled with negative energy electrons into account. We will discuss these bizarre effects towards the end of 221B.

## 3 Hyperfine Interaction

We start with the Maxwell's equations

$$
\begin{align*}
\vec{\nabla} \cdot \vec{E} & =4 \pi \rho  \tag{26}\\
\vec{\nabla} \times \vec{B} & =\frac{1}{c} \dot{\vec{E}}+\frac{4 \pi}{c} \vec{\jmath}  \tag{27}\\
\vec{\nabla} \times \vec{E} & =-\frac{1}{c} \dot{\vec{B}}  \tag{28}\\
\vec{\nabla} \cdot \vec{B} & =0 \tag{29}
\end{align*}
$$

They are derived from the action

$$
\begin{equation*}
S=\int d t d^{3} x\left[\frac{1}{8 \pi}\left(\vec{E}^{2}-\vec{B}^{2}\right)-\phi \rho+\frac{1}{c} \vec{A} \cdot \vec{\jmath}\right] \tag{30}
\end{equation*}
$$

A magnetic moment couples to the magnetic field with the Hamiltonian $H=-\vec{\mu} \cdot \vec{B}$, and therefore appears in the Lagrangian as $L=+\vec{\mu} \cdot \vec{B}$. We add this term to the above action

$$
\begin{equation*}
S=\int d t d^{3} x\left[\frac{1}{8 \pi}\left(\vec{E}^{2}-\vec{B}^{2}\right)-\phi \rho+\frac{1}{c} \vec{A} \cdot \vec{\jmath}+\vec{\mu} \cdot \vec{B} \delta(\vec{x}-\vec{y})\right], \tag{31}
\end{equation*}
$$

where $\vec{y}$ is the position of the magnetic moment. The equation of motion for the vector potential is obtained by varying the action with respect to $\vec{A}$,

$$
\begin{equation*}
\vec{\nabla} \times \vec{B}=\frac{1}{c} \dot{\vec{E}}+\frac{4 \pi}{c} \vec{\jmath}-4 \pi \mu \times \vec{\nabla} \delta(\vec{x}-\vec{y}) . \tag{32}
\end{equation*}
$$

In the absence of time-varying electric field or electric current, the equation is simply

$$
\begin{equation*}
\vec{\nabla} \times \vec{B}=-4 \pi \mu \times \vec{\nabla} \delta(\vec{x}-\vec{y}) \tag{33}
\end{equation*}
$$

It is tempting to solve it immediately as

$$
\begin{equation*}
\vec{B}=-\vec{\mu} \delta(\vec{x}-\vec{y}), \tag{34}
\end{equation*}
$$

but this misses possible terms of the form $\vec{B} \propto \vec{\nabla} f$ where $f$ is a scalar function.

To solve it, we use Coulomb gauge and write Eq. (33) as

$$
\begin{equation*}
-\Delta \vec{A}=-4 \pi \mu \times \vec{\nabla} \delta(\vec{x}-\vec{y}) \tag{35}
\end{equation*}
$$

Because $\Delta_{|\vec{x}-\vec{y}|}=-4 \pi \delta(\vec{x}-\vec{y})$, we find

$$
\begin{equation*}
\vec{A}(\vec{x})=-\mu \times \vec{\nabla} \frac{1}{|\vec{x}-\vec{y}|}=\vec{\mu} \times \frac{\vec{x}-\vec{y}}{|\vec{x}-\vec{y}|^{2}} . \tag{36}
\end{equation*}
$$

The magnetic field is its curl,

$$
\begin{equation*}
\vec{B}(\vec{x})=\vec{\nabla} \times \vec{A}=-\vec{\mu} \Delta \frac{1}{|\vec{x}-\vec{y}|}+\vec{\nabla}(\vec{\mu} \cdot \vec{\nabla}) \frac{1}{|\vec{x}-\vec{y}|} \tag{37}
\end{equation*}
$$

We rewrite the latter term as $\nabla_{i} \nabla_{j}=\left(\nabla_{i} \nabla_{j}-\frac{1}{3} \delta_{i j} \Delta\right)+\frac{1}{3} \delta_{i j} \Delta$ so that the terms in the parenthesis averages out for an isotropic source. They are called the tensor term while the latter the scalar term. Then

$$
\begin{equation*}
\vec{B}(\vec{x})=\vec{\nabla} \times \vec{A}=-\frac{2}{3} \vec{\mu} \Delta \frac{1}{|\vec{x}-\vec{y}|}+\left[\vec{\nabla}(\vec{\mu} \cdot \vec{\nabla})-\frac{1}{3} \vec{\mu} \Delta\right] \frac{1}{|\vec{x}-\vec{y}|} \tag{38}
\end{equation*}
$$

After performing differentiation, we find

$$
\begin{equation*}
\vec{B}(\vec{x})=\frac{8 \pi}{3} \vec{\mu} \delta(\vec{x}-\vec{y})+\frac{1}{r^{3}}\left[3 \frac{\vec{r}}{r} \frac{\vec{\mu} \cdot \vec{r}}{r}-\vec{\mu}\right], \tag{39}
\end{equation*}
$$

where we used the notation $\vec{r}=\vec{x}-\vec{y}$.
Finally the interaction of two magnetic moments, $\vec{\mu}_{1}$ at $\vec{x}$ and $\vec{\mu}_{2}$ at $\vec{y}$, is given by the magnetic field $\vec{B}(\vec{x})$ created by the second magnetic moment at $\vec{y}$

$$
\begin{equation*}
H=-\vec{\mu}_{1} \cdot \vec{B}(\vec{x})=-\frac{8 \pi}{3} \vec{\mu}_{1} \cdot \vec{\mu}_{2} \delta(\vec{x}-\vec{y})-\frac{1}{r^{3}}\left[3 \frac{\vec{\mu}_{1} \cdot \vec{r}}{r} \frac{\vec{\mu}_{2} \cdot \vec{r}}{r}-\vec{\mu}_{1} \cdot \vec{\mu}_{2}\right] . \tag{40}
\end{equation*}
$$

In the MKSA system, it is

$$
\begin{equation*}
H=-\vec{\mu}_{1} \cdot \vec{B}(\vec{x})=-\frac{2 \mu_{0}}{3} \vec{\mu}_{1} \cdot \vec{\mu}_{2} \delta(\vec{x}-\vec{y})-\frac{\mu_{0}}{4 \pi} \frac{1}{r^{3}}\left[3 \frac{\vec{\mu}_{1} \cdot \vec{r}}{r} \frac{\vec{\mu}_{2} \cdot \vec{r}}{r}-\vec{\mu}_{1} \cdot \vec{\mu}_{2}\right] . \tag{41}
\end{equation*}
$$

For hyperfine splittings in the $1 s$ state of the hydrogen atom $Z=1$, the second term vanishes because it is a spherical tensor with $q=2$, and hence only the first term is needed. The magnetic moments are (in MKSA)

$$
\begin{equation*}
\vec{\mu}_{e}=g_{e} \frac{e}{2 m_{e}} \vec{s}_{e}, \quad \vec{\mu}_{p}=g_{p} \frac{|e|}{2 m_{p}} \vec{s}_{p} \tag{42}
\end{equation*}
$$

where $g_{e}=2$ and $g_{p}=2.79 \times 2$. It is useful to define $\mu_{e}=\frac{|e| \hbar}{2 m_{e}}$ and $\mu_{N}=\frac{|e| \hbar}{2 m_{p}}$, and

$$
\begin{equation*}
\vec{\mu}_{e}=-\mu_{e} \frac{2 \vec{s}_{e}}{\hbar}, \quad \vec{\mu}_{e}=2.79 \mu_{N} \frac{2 \vec{s}_{p}}{\hbar} . \tag{43}
\end{equation*}
$$

Therefore the Hamiltonian is

$$
\begin{equation*}
H=+\frac{2 \mu_{0}}{3} 2.79 \mu_{N} \mu_{e} \frac{4}{\hbar^{2}}\left(\vec{s}_{p} \cdot \vec{s}_{e}\right) \delta(\vec{x}) . \tag{44}
\end{equation*}
$$

The first order perturbation of this Hamiltonian gives the hyperfine splitting

$$
\begin{equation*}
E_{h f}=+\frac{2 \mu_{0}}{3} 2.79 \mu_{N} \mu_{e} \frac{4}{\hbar^{2}}\left(\vec{s}_{p} \cdot \vec{s}_{e}\right)|\psi(0)|^{2} \tag{45}
\end{equation*}
$$

with $|\psi(0)|^{2}=\frac{1}{\pi} a_{0}^{-3}$ for the $1 s$ state. Finally, the eigenvalues of the spin operators are

$$
\vec{s}_{p} \cdot \vec{s}_{e}=\frac{1}{2}\left(\left(\vec{s}_{p}+\vec{s}_{e}\right)^{2}-\vec{s}_{p}^{2}-\vec{s}_{e}^{2}\right)= \begin{cases}\frac{\hbar^{2}}{4} & (F=1)  \tag{46}\\ -\frac{3 \hbar^{2}}{4} & (F=0)\end{cases}
$$

Therefore the difference in energies is

$$
\begin{align*}
\Delta E & =+\frac{2 \mu_{0}}{3} 2.79 \mu_{N} \mu_{e} \frac{4}{\hbar^{2}}\left(\frac{\hbar^{2}}{4}-\frac{-3 \hbar^{2}}{4}\right) \frac{1}{\pi a_{0}^{3}} \\
& =\frac{2 \mu_{0}}{3} 2.79 \mu_{N} \mu_{e} \frac{4}{\pi a_{0}^{3}}=\frac{2 \mu_{0}}{3} 2.79 \frac{e \hbar}{2 m_{e}} \frac{e \hbar}{2 m_{p}} \frac{4}{\pi a_{0}^{3}}=9.39 \times 10^{-25} \mathrm{~J} . \tag{47}
\end{align*}
$$

Parametrically, it is $\alpha^{2}\left(m_{e} / m_{p}\right)$ times the binding energy, and hence even more suppressed than the fine structure.

The cosmic thermal bath has $T=2.7 \mathrm{~K}$ and hence $k T=3.7 \times 10^{-23} \mathrm{~J}$, which is much larger than the hyperfine splitting.

## 4 Radio Astronomy

The deexcitation of the $F=1$ states to the $F=0$ state emits a photon of the wavelength 21 cm , and it is called "the 21 cm line." It has had an important impact on astronomy. Because the wavelengh is much longer than typical dust particles, it can bee seen through the dust which blocks photons in the optical range. Because the cosmic thermal bath is "hot enough" to excite the hydrogen to the $F=1$ states, we can see the 21 cm lines even from the region without stars and hot gas. Namely any hydrogen gas emits the 21 cm line. For instance, the spiral arms in our Milky Way galaxy had been discovered using the 21 cm line. Its frequency is 1420.4058 MHz , and hence in the radio range.

The 21 cm line is also seen from other galaxies. In particular, it can be used to measure the rotation speed of hydrogen gas in a given galaxy using the Doppler shifts. It has revealed that the hydrogen gas in the outskirts of spiral galaxies is rotating way too fast to be held together by the gravity of all stars combined. There must be much more mass than what meets the eye. The mysterious dark mass has become known as "Dark Matter." In fact, $23 \%$ of the energy density of the universe is now believed to be the Dark Matter, while the usual atoms, namely electrons, protons, and neutrons, make up only about $4.4 \%$. We are outweighed by more than a factor of five! As far as we know, the Dark Matter is not dim stars. It is believed to be a kind of elementary particle never seen in the laboratory; people are looking for the signal of this particle underground, in space, and using particle accelerators.


Figure 1: Emission of the 21 cm line from a spiral galaxy. Taken from hepph/9712538.


Figure 2: The rotation curve of a spiral galaxy. The dashed line labeled "disk" is the prediction of the rotation speed if the stars in the disk are the only source of gravity to hold the galaxy together. Clearly the disk contribution is not enough. The so-called "halo" of the galaxy which is not made of stars is holding the galaxy together. It shows the evidence for "Dark Matter" that makes up the galactic halos. Taken from hep-ph/9712538.


[^0]:    ${ }^{1}$ It is amusing that the application of the Bohr-Sommerfeld quantization condition leads precisely to the same result.

