

APAS 5110. Atomic and Molecular Processes. Fall 2013.

1. MAGNETIC MOMENT

Classically, the magnetic moment $\boldsymbol{\mu}$ of a system of charges q at positions \mathbf{r} moving with velocities \mathbf{v} is

$$\boldsymbol{\mu} = \frac{1}{2} \sum_{\text{charges } q} q \mathbf{r} \times \mathbf{v} . \quad (1.1)$$

When a magnetic moment $\boldsymbol{\mu}$ is placed in a uniform magnetic field \mathbf{B} , the energy associated is, classically,

$$H_{\boldsymbol{\mu}} = -\boldsymbol{\mu} \cdot \mathbf{B} . \quad (1.2)$$

A point-like magnetic moment $\boldsymbol{\mu}$ itself produces a magnetic field \mathbf{B} given by

$$\mathbf{A} = \nabla \times \left(\frac{\boldsymbol{\mu}}{r} \right) = \frac{\boldsymbol{\mu} \times \hat{\mathbf{r}}}{r^2} , \quad \mathbf{B} = \nabla \times \mathbf{A} = \frac{3\hat{\mathbf{r}}(\boldsymbol{\mu} \cdot \hat{\mathbf{r}}) - \boldsymbol{\mu}}{r^3} \quad (1.3)$$

where \mathbf{A} is the vector potential. If the magnetic moment has finite size, then equation (1.3) gives the magnetic field at distances from the magnetic moment large compared to its size.

For a system of nonrelativistic particles of the same charge q and mass m (for example, electrons in an atom, where $q = -e$ and $m = m_e$) the magnetic moment $\boldsymbol{\mu}$ becomes

$$\boldsymbol{\mu} = \frac{q}{2m} \sum_{\text{ptles}} \mathbf{r} \times \mathbf{p} = \frac{q}{2m} \mathbf{L} \quad (1.4)$$

where \mathbf{L} is the total angular momentum of the particles.

Equation (1.4) motivates the definition of the **Bohr magneton** μ_B (NIST 2018)

$$\mu_B \equiv \frac{e\hbar}{2m_e} = 9.274\,010\,0783(28) \times 10^{-24} \text{ J T}^{-1} = \frac{\alpha}{2} \text{ atomic units} , \quad (1.5)$$

and the **nuclear magneton** μ_N

$$\mu_N \equiv \frac{e\hbar}{2m_p} = 5.050\,783\,7461(15) \times 10^{-27} \text{ J T}^{-1} = \frac{\alpha}{2m_p/m_e} \text{ atomic units} \quad (1.6)$$

with m_p the mass of the proton.

It is found experimentally that particles with spin \mathbf{S} have intrinsic magnetic moments proportional to their spins. For electrons, the **Landé g-factor** g_e is defined by

$$\boldsymbol{\mu}_e = g_e \frac{e}{2m_e} \mathbf{S}_e , \quad (1.7)$$

and is found both theoretically and experimentally to have a value close to -2 , the minus sign coming from the charge $-|e|$ of the electron (NIST 2018),

$$g_e = -2.002\,319\,304\,362\,56(35) . \quad (1.8)$$

For nuclei, the Landé g -factor g_{nuc} is customarily defined as the ratio of the magnetic moment to the spin of the nucleus, with the magnetic moment measured in nuclear magnetons,

$$\boldsymbol{\mu}_{\text{nuc}} = g_{\text{nuc}} \frac{e}{2m_p} \mathbf{S}_{\text{nuc}} . \quad (1.9)$$

2. PARTICLES IN AN ELECTROMAGNETIC FIELD

A powerful discovery of modern physics is that electromagnetism is a local gauge theory based on the group $U(1)$ of rotations about a circle. In the theory, one supposes that elements of the group $U(1)$ act on wavefunctions, rotating them by

$$\psi \rightarrow e^{-iq\theta} \psi \quad (2.1)$$

where q is the charge of the particle in dimensionless units $\hbar = c = 1$ (the charge q in (2.1) is really the dimensionless quantity $q/(\hbar c)^{1/2}$), and $e^{-iq\theta} \in U(1)$ is a rotation. θ being some angle. Electromagnetism emerges miraculously from the requirement that equations of motion must remain invariant when the gauge is rotated by an angle $\theta(t, \mathbf{x})$ which is allowed to vary arbitrarily over time t and space \mathbf{x} . The required gauge invariance is accomplished by defining gauge-covariant derivatives D/Dt and $D/D\mathbf{x}$ to have the property that when the wavefunction ψ undergoes a gauge rotation (2.1) by $e^{-iq\theta}$, the covariant derivatives are similarly rotated by $e^{-iq\theta}$:

$$\frac{D}{Dt} e^{-iq\theta} \psi = e^{-iq\theta} \frac{D\psi}{Dt}, \quad \frac{D}{D\mathbf{x}} e^{-iq\theta} \psi = e^{-iq\theta} \frac{D\psi}{D\mathbf{x}}. \quad (2.2)$$

The property (2.2) is equivalent to requiring that the covariant derivatives commute with a gauge rotation

$$\left[\frac{D}{Dt}, e^{-iq\theta} \right] = 0, \quad \left[\frac{D}{D\mathbf{x}}, e^{-iq\theta} \right] = 0. \quad (2.3)$$

To achieve gauge invariance, one introduces the electromagnetic potentials ϕ , \mathbf{A} , and defines the gauge-covariant derivatives D/Dt , $D/D\mathbf{x}$ by (again in units $\hbar = c = 1$)

$$i \frac{D}{Dt} \equiv i \frac{\partial}{\partial t} - q\phi, \quad -i \frac{D}{D\mathbf{x}} \equiv -i \frac{\partial}{\partial \mathbf{x}} - q\mathbf{A}. \quad (2.4)$$

The covariant derivatives (2.4) commute with a gauge transformation $e^{-iq\theta}$, equation (2.1), provided that under such a gauge transformation the potentials ϕ and \mathbf{A} simultaneously change according to

$$\phi \rightarrow \phi - \frac{\partial \theta}{\partial t}, \quad \mathbf{A} \rightarrow \mathbf{A} + \frac{\partial \theta}{\partial \mathbf{x}}. \quad (2.5)$$

Thus in the quantum mechanical $U(1)$ gauge theory of electromagnetism, equations of motion of particles in an electromagnetic field are obtained by replacing the energy and momentum operators, which are the derivatives with respect to time and space, by the corresponding gauge-covariant operators

$$i\hbar \frac{\partial}{\partial t} \rightarrow i\hbar \frac{\partial}{\partial t} - q\phi, \quad \mathbf{p} \rightarrow \mathbf{p} - \frac{q}{c} \mathbf{A} \quad (2.6)$$

where now proper units have been reintroduced. The Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{p^2}{2m} \psi \quad (2.7)$$

for a free particle mass m is thus changed in the presence of an electromagnetic field ϕ , \mathbf{A} to the Schrödinger equation $i\hbar \partial \psi / \partial t = H\psi$ with Hamiltonian

$$H = \frac{1}{2m} \left(\mathbf{p} - \frac{q}{c} \mathbf{A} \right)^2 + q\phi. \quad (2.8)$$

The Hamiltonian (2.8) is valid for scalar particles, those with zero spin. However, particles of spin $\frac{1}{2}$ are described by the **Dirac equation**. In the nonrelativistic limit, the Dirac equation for spin $\frac{1}{2}$ particles of charge q (for an electron, $q = -e$) moving in an electromagnetic field is the **Pauli equation**

$$H = \frac{1}{2m} \left(\mathbf{p} - \frac{q}{c} \mathbf{A} \right)^2 + q\phi - \frac{q}{m} \mathbf{S} \cdot \mathbf{B} , \quad (2.9)$$

which differs from the scalar Hamiltonian by the last term, in which \mathbf{S} is the spin operator, and $\mathbf{B} \equiv \nabla \times \mathbf{A}$ is the magnetic field.

For a weak, uniform magnetic field, the vector potential is $\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}$. In this case the Hamiltonian (2.9) reduces to

$$H = \frac{p^2}{2m} + q\phi - \frac{q}{2m} (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B} . \quad (2.10)$$

Since an isolated electron has spin $\frac{1}{2}$, one might have thought that electron would have an intrinsic magnetic moment of minus one Bohr magneton. Equation (2.10) however shows that a free electron, charge $-e$, in an external magnetic field has magnetic moment

$$\boldsymbol{\mu}_e = \frac{-e\hbar}{m_e} \quad (2.11)$$

which is twice the expected value. The factor of 2 in front of the spin shows that the Landé g-factor of the electron is $g_e = -2$. This has consequences amply confirmed by experiment:

- the fine-structure energy splittings in atoms;
- electron spin precesses twice as fast as it ‘should’ in an externally applied magnetic field (Stern-Gerlach experiment).

3. ZEEMAN EFFECT

In the presence of a uniform external magnetic field $\mathbf{B} = B\hat{z}$ directed along say the z -direction, the atomic Hamiltonian is perturbed by

$$H_Z = \frac{eB}{2m_e} (L_z + 2S_z) \quad (3.1)$$

in accordance with equation (2.10). The associated perturbation in the energy is

$$\Delta E_Z = \frac{eB}{2m_e} \langle \psi | L_z + 2S_z | \psi \rangle . \quad (3.2)$$

The perturbation (3.2) in the energy involves the average value of the operator $L_z + 2S_z = J_z + S_z$, where $\mathbf{J} \equiv \mathbf{L} + \mathbf{S}$ is the total angular momentum. Now the isotropy of space is broken by the magnetic field, but isotropy is preserved about the direction \hat{z} of the magnetic field. Thus J_z is conserved, with a definite value $M_J\hbar$. However, S_z is not in general conserved, so that

$$\langle \psi | L_z + 2S_z | \psi \rangle = M_J\hbar + \langle \psi | S_z | \psi \rangle . \quad (3.3)$$

In practice, two cases can be distinguished, according to whether the Zeeman energy splitting ΔE_Z of levels in an atom is small or large compared to the fine-structure splitting, ΔE_{FS} .

3.1. Zeeman Effect: Weak Magnetic Field.

If the magnetic field is sufficiently weak that the Zeeman energy splitting of levels in an atom is small compared to fine-structure splitting

$$\Delta E_Z \ll \Delta E_{\text{FS}} , \quad (3.4)$$

then the behavior of the orbital and spin angular momenta can be characterized as follows:

- (1) spin-orbit interaction causes the orbital angular momentum \mathbf{L} and spin \mathbf{S} to precess about the axis of total angular momentum \mathbf{J} ;
- (2) the orbital angular momentum \mathbf{J} precesses, at a much slower rate, about the direction z of the magnetic field.

The precessions preserve \mathbf{L}^2 , \mathbf{S}^2 , and \mathbf{J}^2 . The relatively rapid precession of the spin \mathbf{S} about the axis of total angular momentum \mathbf{J} means that the average value of the spin operator is equal to its value projected along \mathbf{J} ,

$$\langle \psi | \mathbf{S} | \psi \rangle = \left\langle \psi \left| \frac{(\mathbf{J} \cdot \mathbf{S}) \mathbf{J}}{\mathbf{J}^2} \right| \psi \right\rangle \quad (3.5)$$

and in particular the mean value of the z -component of the spin is

$$\langle \psi | S_z | \psi \rangle = \left\langle \psi \left| \frac{(\mathbf{J} \cdot \mathbf{S}) J_z}{\mathbf{J}^2} \right| \psi \right\rangle . \quad (3.6)$$

Equation (3.6) can be reduced by the trick

$$\mathbf{J}^2 = (\mathbf{L} + \mathbf{S})^2 = \mathbf{L}^2 + 2\mathbf{L} \cdot \mathbf{S} + \mathbf{S}^2 \quad (3.7)$$

whence

$$\mathbf{J} \cdot \mathbf{S} = \mathbf{L} \cdot \mathbf{S} + \mathbf{S}^2 = \frac{1}{2} (\mathbf{J}^2 - \mathbf{L}^2 + \mathbf{S}^2) \quad (3.8)$$

so that

$$\langle \psi | S_z | \psi \rangle = \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \hbar M_J . \quad (3.9)$$

It follows that the Zeeman energy splitting is

$$\Delta E_Z = g_Z \frac{e \hbar B M_J}{2m_e} \quad (3.10)$$

with Landé g -factor g_Z

$$g_Z = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} . \quad (3.11)$$

In the particular case that $S = 0$, so $J = L$, then $g_Z = 1$. Likewise if $L = 0$, so $J = S$, then $g_Z = 2$.

Equation (3.10) shows that the $2J + 1$ components of each J level are uniformly split, with energy spacing $g_Z e \hbar B / (2m_e)$.

3.2. Zeeman Effect: Strong Magnetic Field.

The opposite limit where the Zeeman energy splitting is large compared to fine-structure splitting

$$\Delta E_Z \gg \Delta E_{\text{FS}} , \quad (3.12)$$

is called the **Paschen-Back** effect. Here the magnetic field is sufficiently strong that the orbital and spin angular momenta \mathbf{L} and \mathbf{S} precess separately about the direction $\hat{\mathbf{z}}$ of the magnetic field, with spin-orbit interaction causing only a mild perturbation. In this case the z -components of the orbital and spin angular momenta are separately conserved to a good approximation, so that M_L and M_S are good quantum numbers. The precessions preserve \mathbf{L}^2 , \mathbf{S}^2 , but they no longer preserve \mathbf{J}^2 (unless $L = 0$ or $S = 0$), so J is not a good quantum number, even though $M_J = M_L + M_S$ is. In place of (3.9), the mean value of S_z is just

$$\langle \psi | S_z | \psi \rangle = M_S \hbar . \quad (3.13)$$

The Zeeman energy splitting is then given by

$$\Delta E_Z = \frac{e\hbar B (M_J + M_S)}{2m_e} \quad (3.14)$$

which is equation (3.10) with Landé g -factor

$$g_Z = 1 + \frac{M_S}{M_J} . \quad (3.15)$$

According to the usual electric dipole selection rules, permitted transitions between two Zeeman-split LS terms (which must of course belong to different electronic configurations, because parity must change), must satisfy $\Delta M_J = 0$ or ± 1 and $\Delta M_S = 0$. These rules are of course valid for both weak and strong magnetic fields.

4. FINE-STRUCTURE

To next order in powers of $1/c$, the Dirac equation yields the Hamiltonian

$$H = \frac{p^2}{2m} + q\phi - \frac{q}{m} \mathbf{S} \cdot \mathbf{B} - \frac{p^4}{8m^3c^2} + \frac{q}{2m^2c^2} \mathbf{S} \cdot \nabla\phi \times \mathbf{p} + \frac{e\hbar^2}{8m^2c^2} \nabla^2\phi \quad (4.1)$$

The last three terms are relativistic corrections. Of these three terms, the first is the correction to the dependence of relativistic energy on momentum, i.e. it's the next order in the expansion of $[(p^2 + m^2c^2)^{1/2} - m^2c^2] / 2m$; the second is the **spin-orbit** interaction energy; and the last is known as the **Darwin term**, is caused by zitterbewegung, and results in the **Lamb shift**.

For a spherically symmetric potential ϕ , the gradient of the potential is

$$\nabla\phi = \frac{\mathbf{r}}{r} \frac{\partial\phi}{\partial r} \quad (4.2)$$

so the spin-orbit term of the Hamiltonian is

$$H_{\text{spin-orbit}} = \frac{q}{2m^2c^2} \frac{\partial\phi}{r\partial r} \mathbf{S} \cdot \mathbf{r} \times \mathbf{p} = \frac{q}{2m^2c^2} \frac{\partial\phi}{r\partial r} \mathbf{S} \cdot \mathbf{L} . \quad (4.3)$$

The potential of a multi-electron atom with $L \neq 0$ is not spherically symmetric about the nucleus; but it is spherically symmetric in the hydrogenic approximation, and it remains approximately spherically symmetric when the electrostatic repulsion between electrons is

included. The electrostatic field of the electron cloud screens the charge of the nucleus, reducing the effective field experienced by electrons at larger radii from the nucleus. The approximation in which the electrons self-consistently orbit in the spherically symmetric screened potential of the nucleus and its electron cloud is called the **self-consistent field** model of the atom.

In the approximation of a spherically symmetric potential, the perturbation in energy caused by spin-orbit interaction, equation (4.3) with $q \rightarrow -e$ and $m \rightarrow m_e$, is given by

$$\Delta E_{\text{spin-orbit}} = -\frac{e\hbar^2}{4m_e^2c^2} \left\langle \psi \left| \frac{\partial\phi}{r\partial r} \right| \psi \right\rangle [J(J+1) - L(L+1) - S(S+1)] \quad (4.4)$$

the angular part following from the trick (3.7), $\mathbf{S} \cdot \mathbf{L} = \frac{1}{2}(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$. Equation (4.4) shows that the fine-structure levels J of a given LS term are split by

$$\Delta E_{J+1} - \Delta E_J \propto J + 1 . \quad (4.5)$$

The linearly increasing spacing (4.5) of energy levels with J is called the **Landé interval rule**.

5. HYPERFINE SPLITTING OF THE GROUND LEVEL OF HYDROGEN

Hyperfine structure in an atom is caused by the interaction between the magnetic moments of the nucleus and of the electrons. This interaction causes a hyperfine energy shift

$$\Delta E_{\text{HFS}} = \langle \psi | -\boldsymbol{\mu}_e \cdot \mathbf{B}_p | \psi \rangle \quad (5.1)$$

in first order perturbation theory. Because the nucleus is very small, the dipole approximation to the magnetic field \mathbf{B}_p produced by the nucleus at a position $\mathbf{r} = r\hat{\mathbf{r}}$ is good:

$$\mathbf{B}_p = \frac{3\hat{\mathbf{r}}(\boldsymbol{\mu}_p \cdot \hat{\mathbf{r}}) - \boldsymbol{\mu}_p}{r^3} . \quad (5.2)$$

In the ground state of hydrogen, where the orbital angular momentum is zero, the magnetic moment $\boldsymbol{\mu}_e$ of the electron comes entirely from its spin

$$\boldsymbol{\mu}_e = \mu_e \frac{\mathbf{S}_e}{\hbar/2} = \mu_e \boldsymbol{\sigma}_e , \quad \mu_e = g_e \frac{e\hbar}{4m_e} = \frac{g_e}{2} \mu_B . \quad (5.3)$$

The dimensionless operator $\boldsymbol{\sigma} = \mathbf{S}/(\hbar/2)$ denotes Pauli matrices, equations (5.20), and is the same as the spin operator \mathbf{S} but without the $\hbar/2$ factor for the eigenvalue. The magnetic moment of the nucleus, a proton, is

$$\boldsymbol{\mu}_p = \mu_p \frac{\mathbf{S}_p}{\hbar/2} = \mu_p \boldsymbol{\sigma}_p , \quad \mu_p = g_p \frac{e\hbar}{4m_p} = \frac{g_p}{2} \mu_N . \quad (5.4)$$

The g_e and g_p in equations (5.3) and (5.4) are the Landé g -factors of the electron and proton (NIST 2018)

$$g_e = -2.002\,319\,304\,362\,56(35) , \quad g_p = +5.585\,694\,6893(16) . \quad (5.5)$$

Thus the hyperfine energy shift is

$$\Delta E_{\text{HFS}} = \mu_e \mu_p \left\langle \psi \left| \frac{\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p - 3\boldsymbol{\sigma}_e \cdot \hat{\mathbf{r}} \boldsymbol{\sigma}_p \cdot \hat{\mathbf{r}}}{r^3} \right| \psi \right\rangle . \quad (5.6)$$

In equation (5.6), $\boldsymbol{\sigma}_p$ acts only on the spin part of the proton wave function, $\boldsymbol{\sigma}_e$ acts only on the spin part of the electron wave function, $\hat{\mathbf{r}}$ acts only on the angular part of the electron wave function, and r acts only on the radial part of the electron wave function. For the ground state of hydrogen, the relevant wave function is

$$\psi = R_{10}(r)Y_{00}(\hat{\mathbf{r}})\chi_{\text{spin}} , \quad (5.7)$$

where the spin part χ_{spin} of the wave function is, for the spin singlet,

$$\chi_{\text{spin}} = \frac{1}{\sqrt{2}}(\uparrow_e\downarrow_p - \downarrow_e\uparrow_p) . \quad (5.8)$$

and, for the spin triplet,

$$\chi_{\text{spin}} = \begin{cases} \uparrow_e\uparrow_p , \\ \frac{1}{\sqrt{2}}(\uparrow_e\downarrow_p + \downarrow_e\uparrow_p) , \\ \downarrow_e\downarrow_p . \end{cases} \quad (5.9)$$

Now the quantity $\boldsymbol{\sigma}_e \cdot \hat{\mathbf{r}} \boldsymbol{\sigma}_p \cdot \hat{\mathbf{r}}$ in equation (5.6) contains cross terms like $\hat{r}_x\hat{r}_y$ as well as diagonal terms like $\hat{r}_x\hat{r}_x$. The cross terms necessarily average to zero because of the spherical symmetry of the ground state orbital wavefunction

$$\langle Y_{00}|\hat{r}_x\hat{r}_y|Y_{00}\rangle = 0 . \quad (5.10)$$

This leaves the diagonal terms. In view of spherical symmetry,

$$\langle Y_{00}|\hat{r}_x^2|Y_{00}\rangle = \langle Y_{00}|\hat{r}_y^2|Y_{00}\rangle = \langle Y_{00}|\hat{r}_z^2|Y_{00}\rangle = \langle Y_{00}|\frac{\hat{r}^2}{3}|Y_{00}\rangle = \frac{1}{3} . \quad (5.11)$$

Hence

$$\langle Y_{00}|\boldsymbol{\sigma}_e \cdot \hat{\mathbf{r}} \boldsymbol{\sigma}_p \cdot \hat{\mathbf{r}}|Y_{00}\rangle = \frac{1}{3}\langle Y_{00}|\sigma_{e,x}\sigma_{p,x} + \sigma_{e,y}\sigma_{p,y} + \sigma_{e,z}\sigma_{p,z}|Y_{00}\rangle = \frac{\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p}{3} . \quad (5.12)$$

It follows that

$$\langle Y_{00}|\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p - 3\boldsymbol{\sigma}_e \cdot \hat{\mathbf{r}} \boldsymbol{\sigma}_p \cdot \hat{\mathbf{r}}|Y_{00}\rangle = 0 , \quad (5.13)$$

so it looks like the hyperfine energy shift ΔE_{HFS} from equation (5.6) should be zero! This conclusion is not quite true, however, since the $1/r^3$ piece in equation (5.6) leads to a divergence at the origin, so it is possible that there may remain some finite contribution to ΔE_{HFS} at the origin. The source of the difficulty is the $\hat{\mathbf{r}}$ operator, which is not well-defined at the origin, so let me try to get rid of it. Now $\mathbf{B} = \nabla \times \mathbf{A}$ where \mathbf{A} is the vector potential, so

$$-\boldsymbol{\mu}_e \cdot \mathbf{B}_p = -\boldsymbol{\mu}_e \cdot \nabla \times \mathbf{A}_p = \nabla \cdot \boldsymbol{\mu}_e \times \mathbf{A}_p = \nabla \cdot \frac{\boldsymbol{\mu}_e \times (\boldsymbol{\mu}_p \times \hat{\mathbf{r}})}{r^2} , \quad (5.14)$$

where the last step is appropriate for a dipole magnetic field. Since $\hat{\mathbf{r}}/r^2 = -\nabla(1/r)$, equation (5.14) can be written as

$$-\boldsymbol{\mu}_e \cdot \mathbf{B}_p = -\nabla \cdot \boldsymbol{\mu}_e \times (\boldsymbol{\mu}_p \times \nabla(1/r)) = \boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p \nabla^2(1/r) - (\boldsymbol{\mu}_e \cdot \nabla)(\boldsymbol{\mu}_p \cdot \nabla)(1/r) . \quad (5.15)$$

The term $\nabla^2(1/r) = -4\pi\delta(\mathbf{r})$ in equation (5.15) is a delta function at the origin. The other piece $(\boldsymbol{\mu}_e \cdot \nabla)(\boldsymbol{\mu}_p \cdot \nabla)(1/r)$ in equation (5.15) contains cross terms like $\nabla_x\nabla_y(1/r) = 3\hat{r}_x\hat{r}_y/r^3$ as well as diagonal terms like $\nabla_x\nabla_x(1/r)$. The cross terms must still vanish symmetrically,

as in equation (5.10), notwithstanding the divergence at the origin. In view of spherical symmetry,

$$\begin{aligned} \langle R_{10}Y_{00}|\nabla_x^2(1/r)|R_{10}Y_{00}\rangle &= \langle R_{10}Y_{00}|\nabla_y^2(1/r)|R_{10}Y_{00}\rangle = \langle R_{10}Y_{00}|\nabla_z^2(1/r)|R_{10}Y_{00}\rangle \\ &= \langle R_{10}Y_{00}|\frac{\nabla^2(1/r)}{3}|R_{10}Y_{00}\rangle = \langle R_{10}Y_{00}|-\frac{4\pi}{3}\delta(\mathbf{r})|R_{10}Y_{00}\rangle . \end{aligned} \quad (5.16)$$

So the correct expression for the hyperfine energy shift is

$$\begin{aligned} \Delta E_{\text{HFS}} &= \mu_e\mu_p \langle \psi | -\frac{8\pi}{3}\delta(\mathbf{r}) \boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p | \psi \rangle \\ &= \mu_e\mu_p \int (R_{10}Y_{00}\chi_{\text{spin}})^* \frac{-8\pi}{3}\delta(\mathbf{r}) \boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p R_{10}Y_{00}\chi_{\text{spin}} d^3r . \end{aligned} \quad (5.17)$$

With $R_{10} = 2e^{-r}$ in atomic units, and $Y_{00} = (4\pi)^{-1/2}$, equation (5.17) reduces to

$$\Delta E_{\text{HFS}} = -\frac{8\mu_e\mu_p}{3a_0^3} \langle \chi_{\text{spin}} | \boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p | \chi_{\text{spin}} \rangle , \quad (5.18)$$

I will now give two separate ways to figure out the matrix elements of $\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p$ in equation (5.18). The first is pedestrian (but educational); the second uses a trick. The first, direct approach is easiest to carry out with $\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p$ expressed in its chiral form

$$\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p = \sigma_{e,z}\sigma_{p,z} + \frac{1}{2}(\sigma_{e,+}\sigma_{p,-} + \sigma_{e,-}\sigma_{p,+}) . \quad (5.19)$$

Note that the chiral components of the Pauli matrices are

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} , \quad \sigma_+ = \sigma_x + i\sigma_y = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix} , \quad \sigma_- = \sigma_x - i\sigma_y = \begin{pmatrix} 0 & 0 \\ 2 & 0 \end{pmatrix} . \quad (5.20)$$

Operating on the singlet, $\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p$ has eigenvalue -3 ,

$$\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p (\uparrow_e\downarrow_p - \downarrow_e\uparrow_p) = -(\uparrow_e\downarrow_p + \downarrow_e\uparrow_p) + \frac{1}{2}(2\downarrow_e 2\uparrow_p - 2\uparrow_e 2\downarrow_p) = -3(\uparrow_e\downarrow_p - \downarrow_e\uparrow_p) \quad (5.21)$$

while operating on the triplet, $\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p$ has eigenvalue 1, for example,

$$\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p \uparrow_e\uparrow_p = \uparrow_e\uparrow_p . \quad (5.22)$$

The fact that $\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p$ is a scalar (independent of rotations of space) implies that it has the same eigenvalue for each of the three triplet components, which you can check explicitly if you like. A cleverer way of finding the eigenvalues of $\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p$ is to write (with $\hbar = 1$ momentarily for simplicity)

$$\boldsymbol{\sigma}_e \cdot \boldsymbol{\sigma}_p = 4\mathbf{S}_e \cdot \mathbf{S}_p = 2[(\mathbf{S}_e + \mathbf{S}_p)^2 - \mathbf{S}_e^2 - \mathbf{S}_p^2] = 2[S(S+1) - S_e(S_e+1) - S_p(S_p+1)] , \quad (5.23)$$

which yields the same eigenvalues as equations (5.21) and (5.22), -3 for the singlet, $+1$ for the triplet. It follows that the singlet hyperfine state lies below the triplet (remember μ_e is negative), and the hyperfine splitting from (5.17) is

$$\Delta E_{\text{HFS}} = \frac{32\mu_e\mu_p}{3a_0^3} = \frac{2g_e g_p \alpha^2}{3m_p/m_e} \text{ atomic units} = 2.162425 \times 10^{-7} \text{ atomic units} . \quad (5.24)$$

The corresponding wavelength is

$$\lambda = \frac{hc}{\Delta E_{\text{HFS}}} = \frac{3\pi m_p/m_e}{g_e g_p \alpha^3} \text{ atomic units} = 21.0705 \text{ cm} , \quad (5.25)$$

which differs from the observed wavelength 21.106 114 054 18(1) cm by about 1 part in 600. I do a bit better if I use the reduced mass instead of the electron mass in the atomic unit. The atomic unit of length is inversely proportional to the atomic unit of mass, so is $1 + m_p/m_e$ larger than the Bohr radius if the reduced mass is used, giving

$$\lambda = 21.0820 \text{ cm} \quad (5.26)$$

which is now out by 1 in 900. Presumably the remaining discrepancy is from of higher order relativistic effects, the above derivation having assumed the nonrelativistic hydrogenic wavefunction.

The 21 cm transition is magnetic dipole, and the transition probability, from equation (3.3) of the notes on Transition Probabilities and Selection Rules, is

$$A_{21 \text{ cm}} = \sum_L \frac{4\omega^3}{3c^3 \hbar} |\langle \phi_L | \boldsymbol{\mu}_e | \phi_U \rangle|^2 . \quad (5.27)$$

In the present case the electron has zero orbital angular momentum \mathbf{L} , so only the electron's spin contributes to the magnetic moment $\boldsymbol{\mu}_e$. Inserting the electron magnetic moment (1.7) into the transition probability (5.27) yields

$$A_{21 \text{ cm}} = 2.88 \times 10^{-15} \text{ s}^{-1} , \quad (5.28)$$

or approximately $1/(10^7 \text{ yr})$.