

Physics 221A
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Notes 21
Hyperfine Structure in Hydrogen
and Alkali Atoms

Hyperfine effects in atomic physics are due to the interaction of the atomic electrons with the electric and magnetic multipole fields of the nucleus (not counting the electric monopole field, which is the Coulomb field). Hyperfine structure occurs on a smaller energy scale than the fine structure, hence the name. The physical origin of hyperfine effects, however, is quite different. In practice, the most important hyperfine effects are those due to the magnetic dipole and electric quadrupole fields of the nucleus. Higher multipole moments of the nucleus are important in nuclear physics, but not usually in atomic physics. In these notes, we concentrate on magnetic dipole hyperfine effects in hydrogen and alkali atoms, in which the the atomic electron interacts with the magnetic dipole field of the nucleus in both its orbital and spin degrees of freedom. This is much like the interaction of an atomic electron with an external magnetic field, except that in the case of hyperfine effects the source of the magnetic field (the nucleus) is a quantum mechanical system in its own right. Therefore the interaction causes the dynamics of the electron to become coupled to that of the nucleus, so that the Hilbert space is enlarged, new quantum numbers arise, and atomic energy levels are split and shifted.

We begin with the nucleus, which we assume to be in its ground state or some long-lived excited state. We denote the spin of the nucleus by \mathbf{I} , so that $I^2 = i(i+1)\hbar^2$. (We reserve the symbol \mathbf{S} for the electron spin.) The nuclear Hilbert space is

$$\mathcal{E}_{\text{nuc}} = \text{span}\{|im_i\rangle, m_i = -i, \dots, i\}. \quad (21.1)$$

In actual stable nuclei, the spin ranges from $i = 0$ to $i = 15/2$.

The nucleus can possess various electromagnetic multipole moments, depending on the value of the spin i . The allowed moments include the following:

Electric monopole	$1 = 2^0$,	
Magnetic dipole	$2 = 2^1$,	
Electric quadrupole	$4 = 2^2$,	(21.2)
Magnetic octupole	$8 = 2^3$,	

etc., which are sometimes referred to as 2^k -pole moments as indicated by the table. There are two rules which govern the allowed multipole moments of a nucleus. The first is that

a 2^k -pole can occur only if $k \leq 2i$. For example, the proton with $i = \frac{1}{2}$ can (and does) possess an electric monopole moment and a magnetic dipole moment, but not an electric quadrupole moment. The deuteron with $i = 1$ can (and does) possess an electric quadrupole moment, but the alpha particle with $i = 0$ can possess only the electric monopole moment. The second rule is that electric 2^k -poles with $k = \text{odd}$ and magnetic 2^k -poles with $k = \text{even}$ are not allowed.

The rule $k \leq 2i$ follows from the transformation properties of the basis kets $|m_i\rangle$ under rotations (we suppress the index i , which is redundant). For suppose we have an operator A which acts on the nuclear Hilbert space. This operator can be expanded in terms of basis operators $|m_i\rangle\langle m'_i|$, according to

$$A = \sum_{m_i, m'_i} |m_i\rangle\langle m_i| A |m'_i\rangle\langle m'_i| = \sum_{m_i, m'_i} A_{m_i m'_i} |m_i\rangle\langle m'_i|, \quad (21.3)$$

where

$$A_{m_i m'_i} = \langle m_i | A | m'_i \rangle. \quad (21.4)$$

But since the kets $|m_i\rangle$ transform under rotations according to the irreducible representation $j = i$, and since the bras $\langle m'_i|$ also transform according to the same irreducible representation, the operator $|m_i\rangle\langle m'_i|$ transforms according to

$$i \otimes i = 0 \oplus \dots \oplus 2i. \quad (21.5)$$

Therefore any operator which acts on the nuclear spin space can be represented as a sum of irreducible tensor operators of order not exceeding $k = 2i$. But the 2^k -pole moment of the nucleus is, in fact, a order- k irreducible tensor operator, so $k \leq 2i$.

As for the second rule, the exclusion of odd electric 2^k -poles and even magnetic 2^k -poles follows from parity conservation. In fact, small parity-violating effects (one must also worry about time-reversal) may allow nuclei and elementary particles to have some of the moments excluded from the table above. For example, the proton or the electron may have an electric dipole moment, but if such moments exist, they are certainly very small. The detection of such moments or the placing of upper bounds on them is an experimental matter which is currently being pursued in this department.

Let us suppose the nucleus has a spin of at least $\frac{1}{2}$, so that a magnetic dipole moment is allowed. As discussed in Notes 13, the magnetic moment $\boldsymbol{\mu}$ of the nucleus is an operator acting on the nuclear Hilbert space which is given by

$$\boldsymbol{\mu} = \frac{g_N \mu_N}{\hbar} \mathbf{I}, \quad (21.6)$$

where $\mu_N = e\hbar/2m_p c$ is the nuclear magneton and g_N the nuclear g -factor. On the other hand, in classical electromagnetic theory, a magnetic moment $\boldsymbol{\mu}$ at the origin gives rise to a dipole magnetic field described by the vector potential,

$$\mathbf{A}(\mathbf{r}) = \frac{\boldsymbol{\mu} \times \mathbf{r}}{r^3} = -\boldsymbol{\mu} \times \nabla \left(\frac{1}{r} \right). \quad (21.7)$$

This vector potential is in the Coulomb gauge, so that $\nabla \cdot \mathbf{A} = 0$. The magnetic field itself is given by

$$\begin{aligned} \mathbf{B}(\mathbf{r}) &= \nabla \times \mathbf{A} = -\boldsymbol{\mu} \nabla^2 \left(\frac{1}{r} \right) + \boldsymbol{\mu} \cdot \nabla \nabla \left(\frac{1}{r} \right) \\ &= 4\pi \delta(\mathbf{r}) \boldsymbol{\mu} + \frac{3(\boldsymbol{\mu} \cdot \mathbf{r})\mathbf{r} - r^2 \boldsymbol{\mu}}{r^5}. \end{aligned} \quad (21.8)$$

The magnetic field is singular at the origin, as indicated by the δ -function; the second term on the right in Eq. (21.7) is also singular at the origin, and contains within it another δ -function contribution. Some care is required in the treatment of this singularity when analyzing hyperfine effects.

We will treat the hyperfine interaction as a perturbation to a single electron system with Hamiltonian,

$$H_0 = \frac{p^2}{2m} + V(r) + H_{FS}, \quad (21.9)$$

where H_{FS} represents the fine structure effects. In hydrogen or hydrogen-like atoms, we take $V(r) = -Ze^2/r$, and in alkali atoms, $V(r)$ is the self-consistent central field effective potential in which the valence electron moves. In the case of hydrogen-like atoms, we may also wish to add a term to take care of the Lamb shift. Such details do not make much difference in the following analysis; the main fact which we use below is that the unperturbed energy eigenstates are $|n\ell j m_j\rangle$, the unperturbed energy levels are $E_{n\ell j}$, and the complete set of commuting observables is (H, L^2, J^2, J_z) . (The Lamb shift causes the energy levels to depend on ℓ in hydrogen-like atoms.)

We must also consider the effect of the nuclear spin degree of freedom on the unperturbed system. This degree of freedom makes no contribution to the unperturbed Hamiltonian H_0 , because with the hyperfine interaction switched off (and in the absence of any external magnetic field) the nuclear spin Hamiltonian is just zero. But the nuclear degree of freedom enlarges the Hilbert space. Previously we have worked with the electron Hilbert space,

$$\mathcal{E}_{\text{elec}} = \mathcal{E}_{\text{elec}}^{\text{orb}} \otimes \mathcal{E}_{\text{elec}}^{\text{spin}}; \quad (21.10)$$

now we must work with the total Hilbert space,

$$\mathcal{E}_{\text{tot}} = \mathcal{E}_{\text{elec}} \otimes \mathcal{E}_{\text{nucl}} = \mathcal{E}_{\text{elec}}^{\text{orb}} \otimes \mathcal{E}_{\text{elec}}^{\text{spin}} \otimes \mathcal{E}_{\text{nucl}}. \quad (21.11)$$

A suitable set of basis kets for the space \mathcal{E}_{tot} is the tensor product basis,

$$|n\ell j m_j\rangle \otimes |i m_i\rangle = |n\ell j m_j m_i\rangle, \quad (21.12)$$

in which we suppress the constant index i in the final form. We will call this basis the uncoupled basis, because angular momenta \mathbf{J} and \mathbf{I} are as yet uncoupled. (Of course, \mathbf{L} and \mathbf{S} have been coupled to make \mathbf{J} .) The complete set of commuting observables in the uncoupled basis are $(H_0, L^2, J^2, J_z, I_z)$. We could add the constant operators S^2 and I^2 to this list.

The atomic electron interacts with the magnetic dipole field both in its orbital and spin degrees of freedom, giving an interaction hamiltonian which we denote by H_{MD} :

$$H_1 = H_{MD} = \frac{e}{mc} \mathbf{A} \cdot \mathbf{p} + \frac{e}{mc} \mathbf{S} \cdot \mathbf{B}, \quad (21.13)$$

where \mathbf{p} is the electron momentum and where \mathbf{S} is the electron spin. The first term in H_{MD} is the orbital contribution, which comes from expanding $(1/2m)(\mathbf{p} + e\mathbf{A}/c)^2$, just as in the Zeeman effect. The second term is the spin contribution, in which we set $g_e = 2$.

It is relatively straightforward to express the orbital part in terms of angular momentum operators; we simply substitute Eq. (21.7) to obtain

$$H_{MD}^{\text{orb}} = \frac{e}{mc} \frac{(\boldsymbol{\mu} \times \mathbf{r}) \cdot \mathbf{p}}{r^3} = \frac{e}{mc} \frac{\boldsymbol{\mu} \cdot \mathbf{L}}{r^3} = \left(\frac{2g_N \mu_N \mu_B}{\hbar^2} \right) \frac{\mathbf{I} \cdot \mathbf{L}}{r^3}. \quad (21.14)$$

The spin part of H_{MD} is harder to deal with because of the singularity at $r = 0$. Therefore we will smooth out this singularity by replacing the point dipole at the origin by a uniformly magnetized sphere of small radius and net dipole moment $\boldsymbol{\mu}$, and then allowing the radius of the sphere to approach zero. When we do this, we will find that the shifts in the atomic energy levels are finite and well behaved.

The problem of a uniformly magnetized sphere is a standard one in electromagnetic theory. Suppose the sphere, centered at the origin, has radius R , volume $V = (4\pi/3)R^3$, and magnetization $\mathbf{M} = \boldsymbol{\mu}/V$. Since \mathbf{M} is the dipole moment per unit volume, and since the vector potential for a single dipole is given by Eq. (21.7), the vector potential produced at a field point \mathbf{r} due to the magnetized sphere is

$$\mathbf{A}(\mathbf{r}) = \int_{\text{vol}} d^3\mathbf{r}' \frac{\mathbf{M} \times (\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} = -\mathbf{M} \times \nabla \int_{\text{vol}} d^3\mathbf{r}' \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right), \quad (21.15)$$

where the integrals are taken over the volume of the sphere. The integral in the final expression is recognized as the electrostatic potential due to a uniformly charged sphere of

unit charge density, and its negative gradient is the corresponding electric field. Thus, by an elementary application of Gauss' theorem, we have

$$-\nabla \int_{\text{vol}} d^3\mathbf{r}' \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) = \begin{cases} \frac{V\mathbf{r}}{R^3}, & r < R, \\ \frac{V\mathbf{r}}{r^3}, & r > R, \end{cases} \quad (21.16)$$

so that

$$\mathbf{A}(\mathbf{r}) = \begin{cases} \frac{\boldsymbol{\mu} \times \mathbf{r}}{R^3}, & r < R, \\ \frac{\boldsymbol{\mu} \times \mathbf{r}}{r^3}, & r > R. \end{cases} \quad (21.17)$$

We see that the exterior solution ($r > R$) is the same as that of the point dipole [cf. Eq. (21.7)], but the interior solution ($r < R$) is smooth and well behaved as $r \rightarrow 0$. The two solutions are continuous at $r = R$. Finally, taking the curl, we obtain

$$\mathbf{B}(\mathbf{r}) = \begin{cases} \frac{2\boldsymbol{\mu}}{R^3}, & r < R, \\ \frac{3(\boldsymbol{\mu} \cdot \mathbf{r})\mathbf{r} - r^2\boldsymbol{\mu}}{r^5}, & r > R. \end{cases} \quad (21.18)$$

Comparing this with Eq. (21.8), we see that the exterior solution agrees with the field of the point dipole, except for the delta function contribution in Eq. (21.8), which vanishes anyway in the exterior region. Again, the interior solution is smooth and well behaved.

As for the interior solution for \mathbf{B} , we note that the function $f(r)$, defined by

$$f(r) = \begin{cases} \frac{1}{R^3}, & r < R, \\ 0, & r > R, \end{cases} \quad (21.19)$$

is highly concentrated in a small region as $R \rightarrow 0$ and has constant integral $4\pi/3$. Therefore

$$\lim_{R \rightarrow 0} f(r) = \frac{4\pi}{3} \delta(\mathbf{r}), \quad (21.20)$$

and the interior solution \mathbf{B}_{int} has the limit,

$$\lim_{R \rightarrow 0} \mathbf{B}_{\text{int}} = \frac{8\pi}{3} \delta(\mathbf{r}) \boldsymbol{\mu}. \quad (21.21)$$

Here we see a δ -function, just as in the first term of Eq. (21.8), but the coefficient is $8\pi/3$ instead of 4π . The reason for the discrepancy is that the second term in Eq. (21.8) also contains a δ -function component, with coefficient $-4\pi/3$. It is not altogether easy to see this in Eq. (21.8), which is why we have introduced the uniformly magnetized sphere.

We can now combine Eqs. (21.13), (21.18) and (21.19), and write out the spin contribution to the interaction Hamiltonian. It is

$$H_{MD}^{\text{spin}} = \frac{2g_N\mu_N\mu_B}{\hbar^2} \begin{cases} \frac{2}{R^3}\mathbf{S}\cdot\mathbf{I} \rightarrow \frac{8\pi}{3}\delta(\mathbf{r})\mathbf{S}\cdot\mathbf{I}, & r < R, \\ \frac{3(\mathbf{S}\cdot\mathbf{r})(\mathbf{I}\cdot\mathbf{r}) - r^2(\mathbf{S}\cdot\mathbf{I})}{r^5}, & r > R, \end{cases} \quad (21.22)$$

where the limiting form as $R \rightarrow 0$ is also shown for the interior part. The term involving the δ -function is called the “Fermi contact term,” because it is only nonzero when the electron and nucleus are in contact with each other ($\mathbf{r} = 0$).

In perturbation theory, we will be sandwiching eigenstates $|n\ell j m_j\rangle$ of the unperturbed Hamiltonian H_0 around H_{MD} . These eigenstates of H_0 are also eigenstates of L^2 , and it is convenient to treat the cases $\ell = 0$ and $\ell \neq 0$ separately. We will only have to deal with diagonal matrix elements in ℓ , since L^2 commutes with the perturbing Hamiltonian. Consider first the case $\ell = 0$. In this case we take the operator H_{MD}^{orb} of Eq. (21.14) to vanish, since \mathbf{L} is a vanishing operator on any subspace in which $\ell = 0$. This is similar to what we did with the spin-orbit term when discussing fine structure effects. This is a somewhat hand-wavey argument, since the expectation value of $1/r^3$ is infinite in the case $\ell = 0$, but if a more careful justification is desired, one can invoke the magnetized sphere model for the orbital term (just as we have done for the spin term), and one will see that expectation values of H_{MD}^{orb} for $\ell = 0$ do indeed vanish.

Therefore we have only a spin contribution in the case $\ell = 0$, consisting of interior and exterior parts as shown in Eq. (21.22). The exterior part vanishes in the case $\ell = 0$, since the integration against the spherically symmetric s -waves produces an average over angles, and since

$$\langle r_i r_j \rangle = \frac{1}{3} \delta_{ij} r^2, \quad (21.23)$$

where the angle brackets represent an average over angles. Therefore only the interior part of the spin term contributes in the case $\ell = 0$.

In the case $\ell \neq 0$, the interior part of the spin term does not contribute, since wave functions $\psi(\mathbf{r})$ go as r^ℓ near $r = 0$, and only an s -wave gives a nonvanishing contribution when integrated against the δ -function in the interior expression. But both the exterior spin part and the whole orbital term contribute when $\ell \neq 0$.

We can summarize these results by writing down an effective H_{MD} operator, to be

used in the cases $\ell = 0$ and $\ell \neq 0$:

$$H_{MD}^{\text{eff}} = \frac{2g_N\mu_N\mu_B}{\hbar^2} \begin{cases} \frac{8\pi}{3}\delta(\mathbf{r})\mathbf{S}\cdot\mathbf{I}, & \ell = 0, \\ \frac{1}{r^3}\mathbf{G}\cdot\mathbf{I}, & \ell \neq 0, \end{cases} \quad (21.24)$$

where

$$\mathbf{G} = \mathbf{L} - \mathbf{S} + \frac{3(\mathbf{S}\cdot\mathbf{r})\mathbf{r}}{r^2}. \quad (21.25)$$

Notice that \mathbf{G} is a vector operator involving only the electron degrees of freedom (orbital as well as spin).

We turn now to the perturbation analysis of H_{MD} . The unperturbed Hamiltonian H_0 is certainly degenerate, because the unperturbed energies $E_{n\ell j}$ are independent of the magnetic quantum numbers m_j and m_i . Therefore a naive application of degenerate perturbation theory in the uncoupled basis will lead to a matrix indexed by these magnetic quantum numbers, of dimensionality $(2j+1)(2i+1)$. Furthermore, this will be a full matrix, because J_z and I_z are not good quantum numbers of the perturbed problem. We can see this by examining commutators, or by noting that H_{MD} is not invariant under either electron rotations or nuclear spin rotations separately. It is, however, invariant under simultaneous rotations of both electron and spin variables, so H_{MD} does commute with both F^2 and F_z , where \mathbf{F} is the grand total angular momentum vector of the whole system,

$$\mathbf{F} = \mathbf{J} + \mathbf{I} = \mathbf{L} + \mathbf{S} + \mathbf{I}. \quad (21.26)$$

This suggests that we use a coupled basis for the perturbation analysis, in which the coupled basis states are eigenvectors of the complete set of commuting observables $(H_0, L^2, J^2, F^2, F_z)$. The vectors of the coupled basis are given in terms of the uncoupled basis vectors by a Clebsch-Gordan expansion,

$$|n\ell j f m_f\rangle = \sum_{m_j, m_i} |n\ell j m_j m_i\rangle \langle j i m_j m_i | f m_f\rangle. \quad (21.27)$$

The perturbing Hamiltonian H_{MD} is diagonal in this coupled basis, and we can effectively deal with nondegenerate perturbation theory (that is, we need examine only diagonal elements, and there is no matrix to diagonalize).

Therefore the energy shifts are given by

$$\Delta E = \langle n\ell j f m_f | H_{MD} | n\ell j f m_f \rangle. \quad (21.28)$$

We consider the case $\ell \neq 0$ first, in which case we must evaluate the matrix element,

$$\langle n\ell j f m_f | \frac{1}{r^3} \mathbf{G} \cdot \mathbf{I} | n\ell j f m_f \rangle. \quad (21.29)$$

We simplify this by invoking the projection theorem, which tell us that a vector operator such as \mathbf{G} , sandwiched between eigenstates of J^2 with the same j value on both sides, can be replaced by an operator proportional to \mathbf{J} :

$$\mathbf{G} \rightarrow \frac{(\mathbf{G} \cdot \mathbf{J})\mathbf{J}}{j(j+1)\hbar^2}. \quad (21.30)$$

Therefore

$$\langle n\ell j m_f | \frac{1}{r^3} \mathbf{G} \cdot \mathbf{I} | n\ell j m_f \rangle = \frac{1}{j(j+1)\hbar^2} \langle n\ell j m_f | \frac{1}{r^3} (\mathbf{G} \cdot \mathbf{J})(\mathbf{J} \cdot \mathbf{I}) | n\ell j m_f \rangle. \quad (21.31)$$

But by Eq. (21.26), we have

$$\mathbf{J} \cdot \mathbf{I} = \frac{1}{2}(F^2 - J^2 - I^2), \quad (21.32)$$

so our matrix element becomes

$$\begin{aligned} & \langle n\ell j m_f | \frac{1}{r^3} \mathbf{G} \cdot \mathbf{I} | n\ell j m_f \rangle \\ &= \frac{f(f+1) - j(j+1) - i(i+1)}{2j(j+1)} \langle n\ell j m_f | \frac{1}{r^3} (\mathbf{G} \cdot \mathbf{J}) | n\ell j m_f \rangle. \end{aligned} \quad (21.33)$$

As for the operator $\mathbf{G} \cdot \mathbf{J}$, we use Eq. (21.25) and multiply it out, finding

$$\begin{aligned} \mathbf{G} \cdot \mathbf{J} &= \left[\mathbf{L} - \mathbf{S} + \frac{3}{r^2} (\mathbf{S} \cdot \mathbf{r}) \mathbf{r} \right] \cdot (\mathbf{L} + \mathbf{S}) \\ &= L^2 - S^2 + \frac{3(\mathbf{S} \cdot \mathbf{r})^2}{r^2} = L^2, \end{aligned} \quad (21.34)$$

where in the second equality we use $\mathbf{r} \cdot \mathbf{L} = 0$, and in the third we use the fact that $S^2 = (3/4)\hbar^2$, and the fact that

$$(\mathbf{S} \cdot \mathbf{r})^2 = \frac{\hbar^2}{4} (\boldsymbol{\sigma} \cdot \mathbf{r})^2 = \frac{\hbar^2}{4} r^2. \quad (21.35)$$

Thus, the final matrix element in Eq. (21.33) becomes

$$\langle n\ell j m_f | \frac{1}{r^3} (\mathbf{G} \cdot \mathbf{J}) | n\ell j m_f \rangle = \ell(\ell+1)\hbar^2 \left\langle \frac{1}{r^3} \right\rangle = \frac{\hbar^2}{a_0^3 n^3} \frac{1}{\ell + \frac{1}{2}}, \quad (21.36)$$

where in the final expression we have evaluated the expectation value of $1/r^3$ for hydrogen and used a_0 for the Bohr radius. Of course, this expectation value must be done numerically in the case of alkali atoms.

Gathering all the pieces together, we have in the case of hydrogen the energy shift due to the nuclear magnetic dipole interaction,

$$\Delta E_{MD} = \frac{2g_N \mu_N \mu_B}{a_0^3 n^3} \frac{f(f+1) - j(j+1) - i(i+1)}{j(j+1)(2\ell+1)}. \quad (21.37)$$

This is in the case $\ell \neq 0$. However, it is easy to show that the same formula also applies in the case $\ell = 0$. Notice that the energy shift depends on the quantum numbers n , ℓ , j , and f , but not (naturally) on m_f . The energy levels now have the form $E_{n\ell j f}$, and are $(2f + 1)$ -fold degenerate. This is the degeneracy expected generically on the basis of rotational invariance alone. We note that the energy increases with f .

The energy shift (21.37) causes the fine structure levels in the Dirac picture to split, giving rise to hyperfine multiplets. The details depend on whether we have ordinary hydrogen with the proton as nucleus, for which $i = \frac{1}{2}$, or deuterium with the deuteron as nucleus, for which $i = 1$. For example, the Dirac $1s_{1/2}$ level in ordinary hydrogen splits into $f = 0$ and $f = 1$ levels, of which the ground state $f = 0$ is now nondegenerate. This level is the true ground state of the hydrogen atom. Similarly, the Dirac $2p_{3/2}$ splits into $f = 1$ and $f = 2$ levels. In deuterium, the Dirac $1s_{1/2}$ level splits into $f = \frac{1}{2}$ and $f = \frac{3}{2}$ levels, and the Dirac $2p_{3/2}$ level splits into $f = \frac{1}{2}$, $f = \frac{3}{2}$ and $f = \frac{5}{2}$ levels.

However, in deuterium, there are also hyperfine effects from the electric quadrupole moment of the nucleus, which we do not consider here. We simply comment that the electric quadrupole field of the nucleus also gives rise to a coupling between the electron and nuclear degrees of freedom, and therefore produces a further modification of the energy levels discussed here. The electric quadrupole moment of the deuteron was first measured by Rabi and coworkers in 1939; the fact that this moment is nonzero is an important clue to the nature of nuclear forces, for it shows that they have a substantial spin dependence and are not purely central. Thus, it turns out that the deuteron wave function is not purely an s -wave, but has a small admixture of a d -wave.

Electric dipole transitions between the various hyperfine levels are of interest. The matrix element governing such transitions is

$$\langle n\ell j f m_f | r_q | n'\ell' j' f' m'_f \rangle, \quad (21.38)$$

which vanishes unless the following selection rules are satisfied:

$$\begin{aligned} m_f &= m'_f + q, \\ \Delta f &= 0, \pm 1 \quad \text{but } f = 0 \rightarrow f = 0 \text{ not allowed,} \\ \Delta j &= 0, \pm 1, \\ \Delta \ell &= \pm 1. \end{aligned} \quad (21.39)$$

All these rules except the exclusion of $\Delta \ell = 0$ come from the Wigner-Eckart theorem, and the exclusion of $\Delta \ell = 0$ comes from parity conservation (as usual). The exclusion of

$f = 0 \rightarrow f = 0$ comes from the fact that $0 \otimes 1 = 1$. The only reason we do not also exclude $j = 0 \rightarrow j = 0$ is that j is half-integral, and cannot take on the value 0.

The hyperfine splitting of the $1s_{1/2}$ level in hydrogen is particularly interesting. The separation between the $f = 0$ and $f = 1$ hyperfine levels is 1.42 GHz, or 21 cm in wavelength units. Electric dipole transitions between these two levels are forbidden by parity, but magnetic dipole transitions are allowed.

The 21 cm line is quite important in radio astronomy. Spiral galaxies typically possess large clouds of atomic hydrogen, which radiate at the 21 cm wavelength. A population of the excited state $f = 1$ is maintained by collisions; the temperatures prevalent in the clouds are high enough that the populations of the ground state $f = 0$ and the first excited state $f = 1$ are determined mostly by the degeneracies (1 for $f = 0$ and 3 for $f = 1$, although there is some effect due to the Boltzmann factor). By measuring Doppler shifts, the state of motion of the clouds can be measured. In this way, it was first proven that the Milky Way is a spiral galaxy. The 21 cm line is also important in absorption spectra, which can be used to determine the temperature of the clouds of atomic hydrogen.

Molecular hydrogen has a completely different hyperfine structure from atomic hydrogen, arising from the spin-spin interaction of the two protons in the molecule. The transitions between the hyperfine levels of molecular hydrogen are in the megahertz range of frequencies, and are not very useful in astrophysics.