Physics 221A
Fall 1996
Notes 20

Fine Structure in Hydrogen
and Alkali Atoms

In these notes we consider the fine structure of hydrogen and alkali atoms, which concerns the small shifting and splitting of energy levels due to the effects of relativity and spin. In addition to its intrinsic interest and importance in atomic physics, the fine structure is interesting as a window on relativistic quantum mechanics. Although the usual Schrödinger equation is fundamentally nonrelativistic, it is possible to fix it up with various terms which contain the first relativistic corrections in a power series in \((v/c)^2\).

We begin with hydrogen. We use atomic units, so that \(m = e = \hbar = 1\), and \(c = 1/\alpha \approx 137\). We ignore the small difference between the true electron mass and the reduced mass. The unperturbed Hamiltonian is

\[
H_0 = \frac{p^2}{2} - \frac{1}{r},
\]

which has energy levels

\[
E_n = -\frac{1}{2n^2},
\]

If we ignore spin, the unperturbed eigenstates are \(|n\ell m_\ell\rangle\), which are \(n^2\)-fold degenerate. Including the spin in the Hamiltonian (20.1) will not change the eigenvalues (20.2), but it will change the eigenkets, which we will write in the form

\[
|n\ell m_\ell\rangle \otimes |s m_s\rangle = |n\ell m_\ell m_s\rangle,
\]

and it will cause the unperturbed eigenvalues (20.2) to become \(2n^2\)-fold degenerate. We will refer to the basis (20.3) as the uncoupled basis, since \(L\) and \(S\) are uncoupled. This basis is an eigenbasis of the complete set of commuting observables \((H_0, L^2, L_z, S_z)\) corresponding to quantum numbers \((n\ell m_\ell m_s)\). The quantum number \(s\) corresponding to the operator \(S^2\) is suppressed, because it is constant \([s = \frac{1}{2}, S^2 = s(s + 1) = \frac{3}{4}]\).

Next we add the fine structure corrections, which include the relativistic kinetic energy correction, the Darwin term, and the spin-orbit term. We write the perturbing Hamiltonian in the form,

\[
H_{FS} = H_{RKE} + H_D + H_{SO},
\]

where

\[
H_{RKE} = -\frac{p^4}{8c^2},
\]

(20.5a)
\[ H_D = \frac{\pi}{2c^2} \delta(r), \quad (20.5b) \]
\[ H_{SO} = \frac{1}{2c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S}. \quad (20.5c) \]

In the spin-orbit term, \( V \) is the potential energy of the unperturbed Hamiltonian, which for hydrogen is
\[ V = -\frac{1}{r}. \quad (20.6) \]

All three of these terms have \( c^2 \) in the denominator. Since \( c = 1/\alpha \) in atomic units, these terms are all of order \( \alpha^2 \) in comparison to the terms of the unperturbed Hamiltonian (20.1). Equivalently, since the velocity of the electron in the ground state of hydrogen is of order \( \alpha c \), the fine structure terms can all be regarded as being of order \( (v/c)^2 \) relative to the unperturbed Hamiltonian, which is the order we expect for the first relativistic corrections to the energy. In the case of hydrogen, these corrections will be of order \( 10^{-4} \) relative to the unperturbed energy levels (20.2).

The proper way to derive the fine structure corrections (20.5) is to expand the Dirac equation in powers of \( v/c \), whereupon the nonrelativistic Hamiltonian (20.1) results at lowest order, and the fine structure terms appear at order \( (v/c)^2 \). We will actually do this in 221B, but for now we will content ourselves with a brief discussion of the meanings of these terms.

As for the relativistic kinetic energy correction, we recall that the energy of a relativistic particle (rest mass plus kinetic energy) is
\[ \sqrt{m^2c^4 + c^2p^2} = mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots, \quad (20.7) \]
where we have expanded the square root in powers of the momentum, assuming \( p/mc \) is small. The first term is the rest mass, the second is the nonrelativistic kinetic energy, and the third is the correction \( H_{RKE} \) of Eq. (20.5a) (with \( m = 1 \) because of atomic units).

As for the spin-orbit term, this has the form,
\[ H_{SO} = -\frac{1}{2} \mathbf{\mu} \cdot \mathbf{B}, \quad (20.8) \]
where \( \mathbf{\mu} \) is the usual magnetic moment of the electron, including the \( g \)-factor, and \( \mathbf{B} \) is the magnetic field produced by the nucleus as seen in the electron rest frame. In the electron rest frame, the nucleus is a positive charge orbiting the electron, which forms a current loop which creates a magnetic field. Alternatively, the magnetic field \( \mathbf{B} \) is the field which results from Lorentz transforming the electric field of the nucleus when we go from the lab frame to the electron frame. The factor of \( 1/2 \) is due to Thomas precession, a purely inertial
effect of special relativity which causes accelerated frames to rotate relative to inertial frames. As usual, inertial effects in a rotating frame can enhance or cancel out the effects of a magnetic field; in the present case, one half of the nuclear magnetic field is cancelled. Thomas precession is explained poorly in most books, but this is not the place to do a better job, since the correct expression for the spin-orbit term, including the Thomas factor of $\frac{1}{2}$, emerges automatically from the Dirac equation. To summarize, the spin-orbit term is the magnetic energy of interaction of the spin with the magnetic field produced by the moving nucleus, corrected for Thomas precession.

Finally, the Darwin term is not as easy to interpret, but we can say that it is due to a certain nonlocality in the nonrelativistic approximation to the Dirac equation. In the Dirac equation itself, the electron interacts with the field locally, but when we take the nonrelativistic approximation, we find that the electron effectively senses the field over a small distance of the order of a Compton wavelength. This smearing produces an energy correction proportional to the Laplacian of the potential $V$, which in the case of hydrogen is proportional to $\delta(r)$. We will examine this in more detail in 221B.

For now we will just use the fine structure corrections as practice in perturbation theory. Since the unperturbed energy levels are degenerate, we must think in terms of degenerate perturbation theory, in which the shifts in the energy levels are the eigenvalues of the matrix of the perturbing Hamiltonian in the eigenspaces of the unperturbed system. In the present case, the unperturbed levels are $2n^2$-fold degenerate, so we will have a $2n^2 \times 2n^2$ matrix. This matrix will be easier to diagonalize in some bases than others.

The following describes a simple procedure for choosing a good basis. To take a specific example, let $H_1$ be some perturbing Hamiltonian, perhaps one of the fine structure terms or perhaps something else. If we use the uncoupled basis (20.3), then the matrix elements of interest are

$$\langle n\ell m_s | H_1 | n\ell' m'_s \rangle,$$

in which the index $n$ labels the degenerate unperturbed eigenspace, and is therefore the same on both sides, while the three quantum numbers $(\ell, m_\ell, m_s)$ label the basis kets within the eigenspace, and are allowed to be different on the two sides. Suppose now that $[L_z, H_1] = 0$. Then we have

$$0 = \langle n\ell m_s | (L_z H_1 - H_1 L_z) | n\ell' m'_s \rangle = (m_\ell - m'_\ell) \langle n\ell m_s | H_1 | n\ell' m'_s \rangle,$$

so either $m_\ell = m'_\ell$ or else the matrix element (20.9) vanishes. This example illustrates a general principle, which is that if an operator commutes with an observable belonging to a complete set of commuting observables, then the operator has diagonal matrix elements.
with respect to the quantum number of the observable in the eigenbasis of the complete set. This rule can often be used in cases where the Wigner-Eckart theorem does not apply. Its importance for degenerate perturbation theory is that in setting up the matrix elements of the perturbing Hamiltonian, we should use an eigenbasis of a complete set of commuting observables in which as many as possible of the observables commute with the perturbing Hamiltonian. If we are lucky or clever, the perturbing Hamiltonian will commute with all members of some complete set of commuting observables, and then its matrix elements will be entirely diagonal. In this case, the eigenvalues are the diagonal elements, and degenerate perturbation theory will have been effectively reduced to nondegenerate perturbation theory.

Therefore in analyzing the fine structure perturbation, we should look for observables which commute with $H_{FS}$. We start with $H_{RKE}$. This is a purely orbital operator, and is furthermore a scalar. Therefore it commutes with $L$, the generator of orbital rotations. Also, since it is purely an orbital operator, it commutes with $S$, which implies that it also commutes with $J = L + S$. Furthermore, since it commutes with these various operators, it commutes with any functions of them as well, including $L^2$, $S^2$ and $J^2$. The term $H_D$ is similar; it is also a purely orbital operator, which is a scalar. (The $\delta$-function can be thought of as the limit of a highly concentrated, rotationally symmetric function centered on $r = 0$, which therefore commutes with $L$.) Therefore $H_D$ also commutes with $L$, $S$, $J$, $L^2$, $S^2$ and $J^2$. However, the term $H_{SO}$ does not commute with either $L$ or $S$, since either purely spatial or spin rotations would rotate one half or the other of the dot product $L \cdot S$, and would not leave the dot product invariant. However, $H_{SO}$ does commute with $J$, which generates overall rotations of the system and which rotates both $L$ and $S$ simultaneously. It also commutes with $L^2$ and $S^2$, because of the commutators, $[L, L^2] = 0$ and $[S, S^2] = 0$, and with $J^2$, because it commutes with $J$.

We see that $H_{RKE}$ and $H_D$ are diagonal in the uncoupled basis (20.3), but that $H_{SO}$ is not. However, all three operators are diagonal in the eigenbasis of the operators $(L^2, S^2, J^2, J_z)$. This suggests that we use the coupled basis for the perturbation treatment, i.e., the basis in which we have combined angular momenta according to $J = L + S$ or $\ell \otimes \frac{1}{2}$, as in Notes 14. Following Eq. (14.27a), we define the coupled basis in terms of the uncoupled basis by

$$|n\ell jm_j\rangle = \sum_{m_\ell, m_s} |n\ell m_\ell m_s\rangle \langle \ell sm_\ell m_s| jm_j\rangle,$$

where the matrix element is a Clebsch-Gordan coefficient, and where we have suppressed the constant quantum number $s = \frac{1}{2}$ in various places.

Since all three fine structure terms are diagonal in the coupled basis, we only need to
compute their diagonal matrix elements and add them up to get the fine structure energy shifts. We begin with $H_{RKE}$ in Eq. (20.5a), for which the desired matrix element is

$$\langle n\ell jm_j | H_{RKE} | n\ell jm_j \rangle = \sum_{m_c, m_s} \sum_{m_c', m_s'} \langle jm_j | \ell sm_c m_s | n\ell m_c m_s \rangle \langle n\ell m_c m_s | H_{RKE} | n\ell m_c' m_s' \rangle \langle \ell sm_c' m_s' | jm_j \rangle,$$  \hspace{1cm} (20.12)

where we have expressed the coupled basis vectors in terms of the uncoupled basis. We do this because $H_{RKE}$, being a purely orbital operator, is easier to evaluate in the uncoupled basis. Because $H_{RKE}$ does not involve the spin, the middle matrix element in Eq. (20.12) becomes

$$\langle n\ell m_c m_s | H_{RKE} | n\ell m_c' m_s' \rangle = \delta_{m_c, m_c'} \langle n\ell m_c | H_{RKE} | n\ell m_c' \rangle,$$  \hspace{1cm} (20.13)

where the last matrix element is purely orbital. In fact, it is the matrix element of a scalar operator with respect to a standard angular momentum basis (under orbital rotations alone), so by Eq. (15.60), the Wigner-Eckart theorem for scalar operators, it is equal to $\delta_{m_c, m_c'}$ times a quantity which is independent of magnetic quantum numbers. That quantity can be regarded as a reduced matrix element, or it can be taken as the given matrix element with some convenient set of magnetic quantum numbers inserted, since the answer doesn’t depend on them anyway. The value zero is convenient, so we have

$$\langle n\ell m_c | H_{RKE} | n\ell m_c' \rangle = \delta_{m_c, m_c'} \langle n\ell 0 | H_{RKE} | n\ell 0 \rangle.$$  \hspace{1cm} (20.14)

When we put Eqs. (20.13) and (20.14) back into Eq. (20.12) and use the orthogonality of the Clebsch-Gordan coefficients [see Eq. (14.30a)], we find simply

$$\langle n\ell jm_j | H_{RKE} | n\ell jm_j \rangle = \langle n\ell 0 | H_{RKE} | n\ell 0 \rangle.$$  \hspace{1cm} (20.15)

We might have guessed this, since $H_{RKE}$ is diagonal in both the coupled and uncoupled basis.

We can now evaluate the final, purely orbital matrix element. We do this by writing

$$H_{RKE} = -\frac{1}{2c^2} T^2 = -\frac{1}{2c^2} (H_0 - V)^2,$$  \hspace{1cm} (20.16)

where $T = p^2/2$ is the kinetic energy. Then we have

$$\langle n\ell jm_j | H_{RKE} | n\ell jm_j \rangle = -\frac{1}{2c^2} \langle n\ell 0 | (H_0^2 - H_0 V - VH_0 + V^2) | n\ell 0 \rangle$$

$$= -\frac{1}{2c^2} \langle n\ell 0 | (E_n^2 - 2E_n V + V^2) | n\ell 0 \rangle.$$  \hspace{1cm} (20.17)
The final expression involves expectation values of powers of $1/r$; the angular integrations are trivial because of the orthonormality of the $Y_{\ell m}$’s, and the remaining integration is over the radial variable $r$. The needed expectation values are

$$
\langle \frac{1}{r} \rangle = \frac{1}{n^2}, \\
\langle \frac{1}{r^2} \rangle = \frac{1}{n^3(\ell + \frac{1}{2})},
$$

which after some algebra give the final answer in the form,

$$
\langle n\ell jm_j | H_{\text{RKE}} | n\ell jm_j \rangle = (-E_n) \frac{\alpha^2}{n^2} \left( \frac{3}{4} - \frac{n}{\ell + \frac{1}{2}} \right),
$$

where we have set $c = 1/\alpha$ and factored out the unperturbed energy $-E_n = 1/2n^2$.

The analysis of the Darwin term $H_D$ of Eq. (20.5b) is similar. Since it is also a purely spatial scalar operator, its matrix element reduces as in Eq. (20.15),

$$
\langle n\ell jm_j | H_D | n\ell jm_j \rangle = \langle n\ell 0 | H_D | n\ell 0 \rangle = \frac{\pi}{2e^2} |\psi_{n\ell 0}(0)|^2,
$$

where the $\delta$-function has allowed us to do the integral. Here

$$
\psi_{n\ell m}(r) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi)
$$

is the normalized energy eigenfunction. But because of the boundary conditions $R_{n\ell}(r) \sim r^\ell$ for small $r$, the answer will be nonzero only for $\ell = 0$ ($s$-waves). Using the property of the hydrogen radial wave functions,

$$
R_{n0}(0) = \frac{2}{n^{3/2}},
$$

we can write the final answer in the form,

$$
\langle n\ell jm_j | H_D | n\ell jm_j \rangle = (-E_n) \frac{\alpha^2}{n} \delta_{\ell 0}.
$$

Finally, we consider the spin-orbit term, $H_{\text{SO}}$ of Eq. (20.5c). Because of the identity,

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

its matrix elements can be written,

$$
\langle n\ell jm_j | H_{\text{SO}} | n\ell jm_j \rangle = \frac{1}{4e^2} [j(j + 1) - \ell(\ell + 1) - s(s + 1)] \langle n\ell jm_j | \frac{1}{r^3} | n\ell jm_j \rangle.
$$

The remaining matrix element is again of a purely spatial scalar operator, which can be reduced to a purely spatial matrix element as in Eq. (20.15). The result becomes the expectation value of $1/r^3$, which in hydrogen is given by

$$
\langle \frac{1}{r^3} \rangle = \frac{1}{n^3(\ell + \frac{1}{2})(\ell + 1)}.
$$
This expectation value diverges for $\ell = 0$. But in that case, the operator $L$ is the zero operator, so we seem to have the form $0/0$ for the energy correction. The proper way to handle this is to smooth out the Coulomb singularity at $r = 0$, whereupon the expectation value of $1/r^3$ does not diverge, and the answer is seen to vanish for $\ell = 0$. Altogether, we can summarize the answer for $\ell \neq 0$ by

$$\langle n\ell j m_j | H_{SO} | n\ell j m_j \rangle = (-E_n) \frac{\alpha^2}{2n} \frac{j(j+1) - \ell(\ell + 1) - \frac{3}{4}}{\ell(\ell + \frac{1}{2})(\ell + 1)}$$

$$= (-E_n) \frac{\alpha^2}{2n} \begin{cases} \frac{1}{(\ell + \frac{1}{2})(\ell + 1)}, & j = \ell + \frac{1}{2}, \\ -\frac{1}{\ell(\ell + \frac{1}{2})}, & j = \ell - \frac{1}{2}. \end{cases} \quad (20.27)$$

All three corrections, Eqs. (20.19), (20.23), and (20.27), are of order $\alpha^2$ times the unperturbed energy levels, as expected. When we add them up to get the total energy shift due to the fine structure terms, the result simplifies after some algebra, and we find

$$\Delta E_{FS} = (-E_n) \frac{\alpha^2}{n^2} \left( \frac{3}{4} - \frac{n}{j + \frac{1}{2}} \right). \quad (20.28)$$

It is interesting to compare this with the results of the Dirac equation. It turns out that the Dirac equation for the hydrogen atom can be solved exactly, with energy levels given by (we revert to Gaussian units)

$$E_{nj} = \frac{mc^2}{\sqrt{1 + \left[ \frac{\alpha}{n - j - \frac{1}{2} + \sqrt{(j + \frac{1}{2})^2 - \alpha^2}} \right]^2}}. \quad (20.29)$$

When this expression is expanded in powers of $\alpha$, we obtain,

$$E_{nj} = mc^2 \left[ 1 - \frac{\alpha^2}{2n^2} + \frac{\alpha^4}{2n^4} \left( \frac{3}{4} - \frac{n}{j + \frac{1}{2}} \right) + O(\alpha^6) \right]. \quad (20.30)$$

The first term in this expansion is the rest mass-energy, $mc^2$, the next contains the non-relativistic Bohr energy levels $-(1/2n^2)(e^2/a_0)$, and the third contains the fine structure corrections (20.28). Each term is of order $\alpha^2$ times the previous term.

In the case of a hydrogen-like atom (nuclear charge $Z$, such as He$^+$, Li$^{++}$, etc.), the above formulas for energy levels are valid with $\alpha$ replaced by $Z\alpha$. Notice that the expansion in powers of $Z\alpha$ becomes rather poor toward the end of the periodic table, so for heavy elements the fine structure corrections are starting to be of the same order of magnitude...
as the nominal nonrelativistic energy levels. For such heavy atoms it does not make sense even to bother with a nonrelativistic treatment; instead, one should start with the Dirac equation.

The energy shifts (20.28) are negative for all values of \( n \) and \( j \), so fine structure effects depress all energy levels. However, smaller values of \( j \) are more strongly depressed, so the total energy (unperturbed plus fine structure) is an increasing function of \( j \). Since the unperturbed levels did not depend on \( j \), fine structure effects have partially resolved the degeneracy in the unperturbed levels, which now have the form \( E_{nj} \) (instead of just \( E_n \)). The levels still do not depend on the magnetic quantum number \( m_j \), as expected on grounds of rotational invariance. Remarkably, however, they are also independent of the quantum number \( \ell \), which means that the hydrogen atom, even including relativistic corrections, still has some extra symmetry which goes beyond rotational invariance.

In first courses on quantum mechanics the spin-orbit term is frequently the only term considered in treatments of the fine structure. It is true that this term alone is responsible for the \( j \)-dependence of the perturbed energy levels, but unless the relativistic kinetic energy and Darwin terms are also included, one misses the fact that the total fine structure energy shifts are independent of \( \ell \). It is something of a surprise that it works out this way, since the three energy terms separately produce energy shifts which do depend on \( \ell \). It is clear from the formula (20.29) that this \( \ell \)-degeneracy persists to all orders in the expansion of the Dirac equation in powers of \( \alpha \).

However, there is no point in expanding the solution of the Dirac equation beyond the fine structure term, because there are other physical effects which are not incorporated into the Dirac equation which are larger than the next term after the fine structure term. Most important of these are the hyperfine effects, discussed in Notes 21, and the Lamb shift. The Lamb shift is a shift in the energy levels of the Dirac picture which is due to the interaction of the electron with the vacuum fluctuations of the quantized electromagnetic field. It has small effects on all the energy levels, and its most notable feature is that the effect is different on levels with the same values of \( n \) and \( j \) but different values of \( \ell \). Thus, including the Lamb shift, the energy levels in hydrogen have the form \( E_{n\ell j} \), and the only degeneracy is that due to rotational invariance. All extra or “accidental” degeneracy is removed. For example, the Lamb shift causes the \( 2p_{1/2} \) level to be depressed about 1.0 GHz relative to the \( 2s_{1/2} \) level. This energy difference can be measured with high accuracy with radio frequency techniques. The detection and theoretical calculation of the Lamb shift was an important milestone in the history of quantum electrodynamics, because it was the first successful application of renormalization theory. We will consider the Lamb shift in more
The standard spectroscopic notation for the states of hydrogen (or other single electron atoms such as hydrogen-like atoms and alkalis) is \( n\ell j \), where \( \ell \) is represented by one of the standard symbols, \( s, p, d, f \), etc. For example, the ground state of hydrogen is the \( 1s_{1/2} \) level. The low lying terms in hydrogen or a hydrogen-like atom are indicated in Fig. 20.1. Also indicated in the figure are the most important electric dipole transitions (transitions involving only small energy differences, such as \( 2p_{3/2} \rightarrow 2s_{1/2} \), are omitted). Allowed electric dipole transitions, \( (n\ell jm_j) \rightarrow (n'\ell'j'm'_j) \), are those for which the matrix element,

\[
\langle n'\ell'j'm'_j | r_q | n\ell jm_j \rangle,
\]

is nonzero, where \( r_q \) is the component of the position operator \( r \) with respect to the spherical basis (15.27). The operator \( r_q \) is a \( k = 1 \) irreducible tensor operator, both under purely spatial rotations, generated by \( \mathbf{L} \), and under rotations of the whole system, generated by \( \mathbf{J} \). Therefore the Wigner-Eckart theorem can be applied twice. When it is applied to purely spatial rotations and combined with parity, it gives the selection rule \( \Delta \ell = \pm 1 \) (\( \Delta \ell = 0 \) would be allowed by the Wigner-Eckart theorem, but is excluded by parity). When the Wigner-Eckart theorem is applied to total rotations, it gives the selection rules \( \Delta j = 0, \pm 1 \) and \( m'_j = m_j + q \). The last, involving magnetic quantum numbers, gives information about the polarization of the photon emitted on transitions from some initial to some final magnetic substate.

Now for a few comments about the alkali atoms. Most of the analysis presented above goes through for the alkali atoms, with \( V(r) \) replaced by the appropriate screened Coulomb
potential. The unperturbed (nonrelativistic) energy levels of the alkalis have the form $E_{n\ell}$, and are already strongly split according to the $\ell$ values because of the non-Coulomb nature of the central force. The three fine structure terms present in hydrogen are also present in the alkalis, but the relativistic kinetic energy and Darwin terms are not very interesting, because they cause only small shifts in the energy levels of $H_0$, without splitting them. These terms are more interesting in hydrogen, because of the degeneracy among the different $\ell$ values. However, the spin-orbit term does split the alkali levels according to their $j$ values, much as in hydrogen, and produces overall energy levels of the form $E_{n\ell j}$. The analysis of the spin-orbit splitting in the alkalis proceeds as with hydrogen up to Eq. (20.25), after which the expectation value of $1/r^3$ must be done numerically. The most famous example of spin-orbit splitting in the alkalis is the $3p$ level of sodium, which splits into the $3p_{1/2}$ and $3p_{3/2}$ levels. The transition from these levels to the ground $3s_{1/2}$ level is the sodium D-line, which is a close doublet.