Notes—Phys623—Spring 2018
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Notes

Tuesday April 10, Thursday April 12: Radiative transitions

Tuesday we considered spontaneous decay of an atom in an excited state, interacting with the quantized electromagnetic field. The field (vector potential) is quantized using the Coulomb (transverse) gauge condition, $\nabla \cdot \vec{A} = 0$. We derived the formula for the differential decay rate,

$$\frac{d\Gamma}{d\Omega} = (\alpha/2\pi)\omega|\mathcal{M}|^2 \tag{1}$$

where

$$\mathcal{M} = \frac{1}{mc}\vec{\epsilon}^{\,*}_{k,\lambda} \cdot \langle B| \sum_i (\vec{p}_i + i\vec{k} \times \vec{S}_i) e^{-i\vec{k}\cdot\vec{x}_i} |A\rangle \tag{2}$$

is the dimensionless matrix element between the initial and final atomic states. This gives the rate for transitions to a particular final atomic state $|B\rangle$ and a particular photon polarization $\vec{\epsilon}_{k,\lambda}$, with the photon wavevector in an infinitesimal solid angle $d\Omega$ around $\vec{k}$. The frequency is given by energy conservation $\hbar\omega = \hbar ck = E_A - E_B$. The sum is over the electrons in the atom.

Multipole expansion

It is often a good approximation to replace the exponential $e^{-i\vec{k}\cdot\vec{x}_i}$ by 1. To see why/when , note that x_i in the atom is of order a/Z for an orbital seeing a nuclear charge, or effective nuclear charge Z, so the exponent is $\sim ka/Z$. The photon energy is $\hbar ck \lesssim Z^2e^2/a$, where the upper bound is for maximal transition energies. So $ka \lesssim Z^2\alpha$, hence $ka/Z \lesssim Z\alpha$. Except for inner shell electrons of high Z atoms, this is much smaller than unity. Hence it makes sense to expand:

$$e^{-i\vec{k}\cdot\vec{x}_i} = 1 - i\vec{k}\cdot\vec{x}_i + O(k^2x_i^2). \tag{3}$$

The 1 term gives the electric dipole matrix element (E1) from the $\vec{p}$ term, and spin magnetic dipole (SM1) from the $\vec{S}$ term in (2). The $\vec{k}\cdot\vec{x}_i$ term gives the electric quadrupole (E2) from the and orbital magnetic dipole (OM1) contributions, from the symmetric and antisymmetric parts of $p_i^a x_i^b$ under ab index permutation.

For the electric dipole, one could work with matrix elements of $\vec{p}_i$, but usually this is re-expressed in terms of the position vectors, using $[H_0, \vec{x}_i] = (-i\hbar/m)\vec{p}_i$, where H_0 is the electronic Hamiltonian. Thus

$$\frac{1}{mc}\langle B|\vec{p}_i|A\rangle = \frac{i}{\hbar c}\langle B|[H_0, \vec{x}_i]|A\rangle = \frac{i(E_B - E_A)}{\hbar c}\langle B|\vec{x}_i|A\rangle = -ik\langle B|\vec{x}_i|A\rangle. \tag{4}$$

Together with (1) and (2), this yields for the E1 transition rate

$$\frac{d\Gamma^{\mathrm{E1}}}{d\Omega} = \frac{\alpha\omega^3}{2\pi c^2}|\vec{\epsilon}^{\,*}_{k,\lambda} \cdot \vec{d}_{BA}|^2, \tag{5}$$

where the dipole matrix element $\vec{d}_{BA}$ is defined by

$$\vec{d}_{BA} = \sum_i \langle B|\vec{x}_i|A\rangle. \tag{6}$$

I'll come back to the other terms in the multipole expansion, but for now let's consider the dipole selection rules. x_i is an odd-parity vector operator with respect to both $\vec{L}$ and $\vec{J}$. So in order for d_{BA} to be nonzero we must have $\Pi_B = -\Pi_A$, and $L_B \subset 1 \otimes L_A$, and $J_B \subset 1 \otimes J_A$. This requires $\Delta L = \pm 1$. $\Delta L = 0$ is excluded by the parity selection rule, and, if $L = 0$ then of course $\Delta L = -1$ is meaningless. For J it requires $\Delta J = 0, \pm 1$, unless $J_A = 0$, in which case only $\Delta J = 1$ is allowed. Transitions not satisfying a selection rule are called "forbidden" for that kind of transition.

Transitions from $J = 0$ to $J = 0$ are "absolutely forbidden" for one-photon transitions. Intuitively, this is because the photon carries angular momentum, but the initial and final atomic states have zero angular momentum, thus violating angular momentum conservation. You should worry that perhaps orbital angular momentum of the photon-atom system could cancel the photon's spin angular momentum, but this isn't possible, since the latter is parallel to $\vec{k}$ whereas the former is perpendicular to $\vec{k}$. For a more computational derivation of this absolutely forbiddeness, note that for rotationally invariant states $|A\rangle$ and $|B\rangle$, the matrix element in (2) must be parallel to $\vec{k}$, so its inner product with the polarization vector vanishes.

Thursday, March 8: Degenerate electron gas, Thomas-Fermi model

Today I discussed the physics of the Thomas-Fermi model of the ground state of an atom, and also explained the physics of the Chandrasekhar limit on the mass of white dwarf and neutron stars.

Thomas-Fermi model

The TF model treats the electrons in the ground state of an atom as a spherically symmetric, degenerate Fermi gas cloud. The key idea is to impose at each point the relation $n = (3\pi^2)^{-1}(p_F/\hbar)^3$ between the number density n and the Fermi momentum p_F, as if one had a uniform density system. p_F in turn can be expressed in terms of the local electrostatic potential V, using the fact that the ground state is stationary: the Fermi kinetic energy plus the electrostatic potential energy must be constant throughout space, otherwise charges could move around to minimize the energy. This allows n to be expressed in terms of V. Finally, V is required to satisfy Poisson's equation, with source given by the nuclear charge density plus the electron charge times n. This results in a second order ordinary differential equation for V which can be solved numerically. The subject is discussed in Schwabl and in

Littlejohn's notes, so I will add here only a few remarks I made that are not in those sources.

- For Ag (silver), [Kr]$4d^{10}5s^1$, the TF energy levels agree with Hartree-Fock calculations to within 1% for the 1s, 2s, and 2p levels, 2% for the 2p level, and 6% for the 4s level.
- One can show that the total Coulomb repulsion energy of the electrons is $-1/7$ times the total Coulomb attraction energy to the nucleus.
- One half the total charge lies within the radius $\sim 1.33Z^{-1/3}a$, where a is the Bohr radius.
- The mean velocity of the electrons scales as $\sim Z^{2/3}\alpha$.
- The approximation is valid in the range $a > r > a/Z$. For large Z, most of the electrons lie in this range.
- The total ionization energy is $\approx 20.8Z^{7/3}$ eV, which compares well with the experimental formula $\simeq 20.8Z^{7/3}$ eV. For ^{26}Fe (iron), $Z^{7/3} \simeq 77$, so the experimental total ionization energy is $\simeq 1.2$keV.

Degenerate stars

If you squeeze a degenerate Fermi gas into a smaller volume, the density goes up, and hence so does the Fermi energy ϵ_F and the total energy. This means the gas has a pressure, called Fermi pressure. A white dwarf star is supported by electron Fermi pressure. This can support any mass against Newtonian gravitational collapse if the nonrelativistic energy-momentum dispersion relation is used. However, if the relativistic one is used, there is a maximum mass that can be supported, which is called the Chandrasekhar mass, and is about $1.44M_\odot$. A white dwarf with the mass of the sun is about as large as the earth. Similarly, a neutron star is supported by neutron Fermi pressure. The maximum mass of a neutron star depends on unknown aspects of the equation of state, but it seems to be around $2M_\odot$. The radius of a neutron star is around 10-12 km.

Here are some rough estimates to support these claims. The gravitational energy is $E_{\rm grav} \sim -GM^2/R \sim -Gm_p^2N^2/R$, where m_p is the proton mass and N is the number of protons. (I'm ignoring all numerical factors.) The nonrelativistic kinetic energy of the Fermi gas of electrons is $E_{\rm F} \sim Np_F^2/m_e$. Now $p_F^2 \sim \hbar^2 n^{2/3} \sim N^{2/3}/R^2$, so the kinetic energy rises faster with R than the gravitational energy falls, and the star is always supported.

Suppose however the Fermi momentum is relativistic, $p_F \gtrsim m_e c$. Then $\epsilon_F = (p_F^2c^2 + m_e^2c^4)^{1/2}$, which at large momentum becomes $\epsilon_F \sim p_F c$, and so the total kinetic energy is $E_{\rm F} \sim Np_Fc \sim N^{4/3}\hbar c/R$. Now since the gravitational energy is $\propto N^2$, while the kinetic energy is only $\propto N^{4/3}$, there is an upper limit for N beyond which the star cannot be supported. This happens when $Gm_p^2N^2 \gtrsim N^{4/3}\hbar c$, i.e. when $N > (\hbar c/G)^{3/2}m_p^{-3}$. Since this must be dimensionless, the quantity $(\hbar c/G)^{1/2}$

must be the Planck mass, $m_{\rm Planck} = 10^{19}{\rm GeV} = 10^{-5}{\rm gm}$. A white dwarf star is thus unstable when the mass is

$$M \sim N m_p \gtrsim \left(\frac{m_{\rm Planck}}{m_p}\right)^2 m_{\rm Planck} \sim 10^{33}{\rm gm} \sim M_\odot. \tag{7}$$

For a neutron star, we replace the electron gas by the neutron gas. Since the electron mass doesn't enter the result, and since the neutron and proton masses are equal to within a tenth of a percent, the result at this level of accuracy is the same. Of course the above were rough estimates dropping factors. Moreover, for neutron stars it is important to take into account general relativity corrections to Newtonian gravity.

We should check that if N takes on the putative maximum value, then the Fermi energy is indeed relativistic, otherwise our estimate is inconsistent. One way to do this is to use the nonrelativistic result to compute the stellar radius, by minimizing the total energy with respect to R. This yields $R = N^{-1/3} m_p^{-2} m_e^{-1}$ in Planck units ($\hbar = c = G = 1$). On the other hand we showed above that the Fermi momentum is $p_F \sim N^{1/3}/R$, so we have $p_F \sim N^{2/3} m_p^2 m_e \sim m_e$, where I've used the result we found above for the maximum N. This estimate thus suggests that the Fermi momentum is becoming relativistic, so that the rough estimate is consistent, but I wouldn't say it's definitive. A more careful computation seems required to draw a definite conclusion, although perhaps just a more clever estimate could be adequate.

Thursday, March 1: Multi-electron atoms

1. The simple product of hydrogenic variational wavefunctions for a proton with two electrons yields an upper bound -0.945 Ry to the ground state energy. Since this is not less than -1 Ry, it is higher that the ionized state, H + e^-, so it fails to reveal the existence of the hydrogen anion, H^-. Challenge: try to find a trial wavefunction that establishes the existence of the bound state. It will presumably need to incorporate correlations between the two electrons, so that the electrons tend to be on opposite sides of the proton...If you find one, please share it with the class.

2. Excited states of helium, as covered in Schwabl. I harped on the fact that while the exchange integral "K" can be shown to be positive, it isn't manifestly positive, and I conjectured that if the Coulomb potential were modified, it might not be positive. For instance: suppose the denominator is replaced by $d + w$, where d is the distance between the electrons (the usual Coulomb denominator), and w is a constant length. This would decrease the advantage of the two electrons avoiding being in the same location, which leads me to suspect that it might invalidate the positivity of the integral. Let me know if you test this (for different w's)...

3. Multi-electron atoms: I tried to summarize the salient points. Many more details, and in particular explanations of the Hartree-Fock method of the self-consistent field approximation, can be found in Schwabl or Littlejohn. I don't plan to delve into those details, but wanted to emphasize a conceptual point:

the ground state, being an energy eigenstate of a rotationally invariant Hamiltonian, must be an eigenstate of F^2 (unless it's degenerate, which it ain't except with respect to the m_F value), hence has a definite total angular momentum quantum number F. To the extent that the hyperfine interaction can be treated as a term proportional to $\vec{I} \cdot \vec{J}$ in the Hamiltonian, it can also be taken to be an eigenstate of J, L and S, but that is only a (very good for many purposes) approximation, valid in first order perturbation theory, but (I think) not in general valid beyond that.

4. I explained the notion of electron configurations and shells, along the lines in Schwabl. I also explained the meaning of the "term symbol" (a.k.a. "spectroscopic symbol"), ${}^{2S+1}L_J$, and how Hund's rules allow you to infer — usually correctly — the term symbol, given the configuration. I explained the example of oxygen, showing it is ${}^3P_2$. I'd like to do another couple of examples here: iron (Fe), and ytterbium (Yb).

5. Example: The configuration of Fe is [Ar]$4s^2 3d^6$. The $4s$ shell is filled but the $3d$ shell has room for $2 \times 5 = 10$ electrons, and contains only 6. To maximize the spin, we can distribute 5 electrons with spin up among the 5 m_l values, and place the 6th electron with spin down in any one of the orbitals. That yields $S = 2$. The maximal m_l would be obtained if we placed the 6th electron in the $m_l = 2$ orbital, yielding a maximal total $m_l = 2$, and therefore $L = 2$ is the maximal L accessible (given that S was already maximized). Finally, since the shell is more than half-filled, we should maximize J given $S = 2$ and $L = 2$, which yields $J = 4$, and therefore the term symbol is ${}^5D_4$.

The states with higher J values but the same L and S are excited states, and it's interesting to inspect the energy differences. You can see them here: `https://physics.nist.gov/PhysRefData/Handbook/Tables/irontable5.htm`. If you compute the energy differences and divide by J, for adjacent levels, $[E(J)-E(J-1)]/J$, you find that they are fairly constant: $-104, -96, -92, -90$, in units of inverse cm. This near-constancy follows from the Landé interval rule. That rule follows from the fact that, in first order perturbation theory, the net effect of the spin-orbit coupling can be seen to be equal, for each configuration and L and S, to an L, S dependent constant times the expectation value of $\vec{L} \cdot \vec{S} = (J^2 - L^2 - S^2)/2 = [J(J+1) - L(L+1) - S(S+1)]/2$. The change of this quantity between J and $J-1$, for fixed L and S, is J. The adjacent energy differences are thus proportional to J, so if you divide them by J, the result should be J independent. As to the magnitude of the energy differences, for instance, between the ground state ($J = 4$) and the next excited state ($J = 3$) the energy goes up by 416 inverse cm. Now 1/cm is about 0.12 meV, so 416/cm is ~ 50 meV. Compared to 10 eV this is 50 $\times 10^{-4}$, which is $\sim 10^{-3}$. This is ~ 10 times larger than the relative size of relativistic corrections in hydrogen. Apparently, as the atomic number grows, spin-orbit coupling strengths do increase, I suppose because the participating electrons are moving faster and/or they are sometimes seeing a larger central charge.

6. The final example I want to mention here is Yb, since a student mentioned using that atom in a quantum computer setting in the lab she works in, and since it is used in the most stable atomic clock. (The quantum computer may use trapped ions not neutral atoms... To read about the clock, see the article linked on the Supplements page.) The ground state configuration is $[\mathrm{Xe}]4f^{14}6s^2$. The letter f denotes $l = 3$, whose shell has $2 \times 7 = 14$ states, so it is a filled shell, which has $S = 0$ and $L = 0$, and the term symbol of the ground state is thus ${}^1S_0$.

The two $6s$ electrons are like in helium, so among the excited states is a spin triplet ($S = 1$) (like orthohelium) that also has orbital angular momentum $L = 1$, and the fine structure of this level includes $J = 0, 1, 2$ sublevels. The $J = 0$ term has term symbol ${}^3P_0$. In this state, the spin and orbital angular momenta are each nonzero but they add to zero. The one-photon transition from this state down to the ground state is "completely forbidden" as we'll see later in the semester, because the ground state also has $J = 0$, and there is no $J = 0$ to $J = 0$ one-photon transition. If that were the whole story the lifetime of this state would be extremely long (years?). That would be the case for one of the $I = 0$ isotopes of ytterbium. However, the long lifetime also means the transition line "width" is extremely narrow, so it is too difficult to excite the transition to be practical. The Yb-171 isotope, on the other hand, has nuclear spin $I = \frac{1}{2}$, and therefore a magnetic dipole moment, which introduces a hyperfine interaction. This means that the ${}^3P_0(F = \frac{1}{2})$ state mixes with the ${}^3P_1(F = \frac{1}{2})$ state, and the latter state has an allowed decay mode. Although not as narrow, it's still a very narrow transition, and correspondingly very long lived, since a spin flip is needed to get from the triplet to the singlet spin state, and since (I presume) the amount of admixture of the latter state is small.

Tuesday Feb. 20: Hyperfine interactions

Today I finished discussing the hyperfine splitting of atomic energy levels. Since I approached the material rather differently than does Schwabl or Littlejohn, I wanted to make a brief synopsis here. The following main points were made:

1. Reviewed definition of gyromagnetic ratio and g-factor.

2. Hyperfine interactions are interactions of nuclear magnetic dipole or electric quadrupole moments with the field produced by the electrons, evaluated at the nucleus. One could also view this the other way around: the influence of nulcear multipole fields on the electron. Either way, it's the interaction energy that matters, and we'll view it the first way.

3. An electric dipole moment (EDM) is forbidden unless the Hamiltonian violates both time reversal symmetry and parity symmetry. (See my Supplement on Nuclear moments.) Parity is strongly violated by the weak interactions, and time reversal symmetry is violated by the complex phases in the quark mixing

matrix of the standard model, but that would be a very small effect in nuclei, so some very small EDM is expected, but none has been detected as yet. The main search is for a neutron EDM. The present upper limit is 10^5 times larger than the value expected from the quark mixing matrix, but other theoretical considerations suggest that there should be a larger value, and finding it could be an important sign of new physics. See the Supplement for a few more details.

4. The nuclear magneton $e_0/(2m_pc)$ is smaller than the Bohr magneton $e_0/(2m_ec)$ by a factor $m_e/m_p \simeq 1/1836 \sim 10^{-3}$.

5. The magnetic hyperfine interaction Hamiltonian is $H_{\rm hf,mag} = -\vec{\mu}_{\rm nucleus}\cdot\vec{B}_{\rm electrons}$, where the electronic magnetic field is evaluated at the nuclear position. Using the Wigner-Eckart theorem, I showed that the expectation value of this Hamiltonian in states of definite $|FIJm_F\rangle$ is equal to the expectation value of $\vec{I}\cdot\vec{J}$, times two factors that depend only on I and J. (Here I and J are the nuclear and electronic total angular momenta, and F is the overall total angular momentum of the atom.) The first factor is the nuclear gyromagnetic ratio. The second factor depends on the electronic state. (The key observation behind the argument is that $\vec{\mu}_{\rm nucleus}$ is a nuclear vector operator and $\vec{B}_{\rm electrons}$ is an electronic vector operator. Using this, we may invoke the aspect of the Wigner-Eckart theorem that states that matrix elements of any two tensor operators of the same rank are proportional to each other.)

6. When treating the hyperfine interaction as a perturbation, we face the fact that the states labeled by different m_I & m_J are degenerate, so we must find the eigenvectors and eigenvalues of the hyperfine Hamiltonian truncated to the degenerate (IJ) subspace. In view of point 5., this is easy, because $\vec{I}\cdot\vec{J} = (F^2 - I^2 - J^2)/2 = [F(F+1) - I(I+1) - J(J+1)]/2$, i.e., $\vec{I}\cdot\vec{J}$ is already diagonal in the $|FIJm_F\rangle$ basis. The level shifts thus have the form $A(I,J)[F(F+1) - I(I+1) - J(J+1)]$.

7. The most fundamental example is the ground state of the hydrogen atom. The unperturbed electronic orbital state is $1s$, and the spin state is arbitrary, while the nuclear spin state is also arbitrary. Both the electron and the proton have spin-1/2, so $I = 1/2$ and $J = 1/2$, hence the possible values of F are 1 and 0, the triplet and singlet. The corresponding values of $[F(F+1) - I(I+1) - J(J+1)]$ are $1/2$ and $-3/2$. It turns out that the coefficient A here is positive, so the ground state is the singlet, which is depressed three times as much as the triplet is raised. The frequency of this transition (i.e. the energy difference divided by hbar) is around 1.4 GHz, and the wavelength is the famous "21 cm line".

8. A super important example to physics is the ground state of Cesium-133. Cesium is an alkalai atom, with a $6s$ valence electron. All the other electrons make up closed shells, which are exactly rotationally invariant, and so contribute nothing to the magnetic moment of the electrons. The nuclear spin

is $I = 7/2$, so the possible values of F are 4 and 3. The energy difference between these is radiation with a frequency around 10 GHz. In fact the SI unit of the second is *defined* to be exactly 9,192,631,770 periods corresponding to this frequency.

9. And now what about electric quadrupole moments? See the Supplement for the definition. The key thing is that the quadrupole moment operator is a rank 2 irreducible tensor operator. Hence the selection rule aspect of the Wigner-Eckart theorem tells us that a spin-1/2 nucleus cannot have an electric quadrupole moment: $\langle \frac{1}{2}|Q_2|\frac{1}{2}\rangle = 0$, because $\frac{1}{2}$ is not in $2 \otimes \frac{1}{2}$. Any nuclear spin greater than 1/2 however does support an electric quadrupole, and in particular the Cs-133 nucleus does. So why don't we need to consider how that affects the fine structure of the ground state of Cs-133? Why can we conclude it is only split into a doublet, corresponding to $F = 4$ and $F = 3$?

The answer, again, comes from the selection rule. To understand this, we should first write down the interaction energy between the nuclear quadrupole moment and the electronic field. I gave an only partly true explanation of this in class, so let me try to fix it here: The electrostatic interaction energy of a charge distribution ρ and an electrostatic field Φ is $\int \rho\Phi dV$. This leads to a quadrupole interaction energy $\frac{1}{2}Q^{ij}\Phi_{,ij}(0)$ (see below for a derivation). Since Q^{ij} is traceless, the trace part of $\Phi_{,ij}(0)$ doesn't contribute here, so we may replace this by

$$\tfrac{1}{2}Q^{ij}W_{ij}, \quad \text{where} \quad W_{ij} = (\Phi_{,ij} - \tfrac{1}{3}\nabla^2\Phi\delta_{ij})(0). \tag{8}$$

W_{ij} is an operator on the electronic Hilbert space, since Φ is generated by the electron(s), and in fact it is an irreducible tensor operator of rank 2. Hence its expectation value vanishes in electronic states with $J = 0$ or $J = 1/2$. In particular, in the case of Cs-133, $\langle 6s|W_{ij}|6s\rangle = 0$. All of which is to say that, although the cesium-133 nucleus has a reasonably large electric quadrupole moment, it can't "feel" the electric field generated by the $6s$ electron!

Derivation of the quadrupolar interaction energy

Let's expand Φ around the origin, taken to be the center of mass of the nucleus, viz,

$$\Phi(x) = \Phi(0) + \Phi_{,i}(0)x^i + \tfrac{1}{2}\Phi_{,ij}(0)x^ix^j + \dots \tag{9}$$

The i and j indices are the cartesian coordinate indices, the comma indicates partial derivative, and repeated indices are summed over. Now we can carry out the interaction energy integral with this expansion, and we get

$$Q\Phi(0) + p^i\Phi_{,i}(0) + \tfrac{1}{2}Q^{ij}\Phi_{,ij}(0) + \tfrac{1}{6}(\int \rho x^2 dV)\nabla^2\Phi(0) + \dots \tag{10}$$

The last term is needed because in order to express $\int \rho x^i x^j dV$ in terms of the quadrupole moment Q^{ij} we must subtract and then add back in the trace

part:

$$\int \rho x^i x^j dV = \int \rho (x^i x^j - \tfrac{1}{3} x^2 \delta^{ij}) dV + \tfrac{1}{3} \delta^{ij} \int \rho x^2 dV. \tag{11}$$

The first term in this expansion (10) corresponds to the Coulomb interaction, the second term is the EDM discussed above, which nearly vanishes, and the third term is the electric quadrupole interaction. The last term is a second moment of the charge distribution, multiplied by the Laplacian of the potential evaluated at the origin. According to Maxwell's equations, the latter is proportional to the electron charge density at the origin. This term represents a nuclear finite size correction to the Coulomb potential, and is a scalar, so it doesn't break the degeneracy among the m_I, m_J states.