

1. As promised, here is the trick for summing the matrix elements for the Stark effect for the ground state of the hydrogen atom.

Recall, we need to calculate the correction to the ground state energy to second order in the perturbation due to an external field. This correction is

$$\Delta E_1 = e^2 E^2 \sum_{m=2}^{\infty} \frac{|\langle m, 1, 0 | z | 1, 0, 0 \rangle|^2}{E_1 - E_m} .$$

To simplify the notation, let's call  $|1, 0, 0\rangle = |0\rangle$ , the ground state with energy  $E_0$  and call  $|m, 1, 0\rangle = |n\rangle$  with energy  $E_n$  and  $n \geq 1$ . So, we want to compute

$$\Delta E_0 = e^2 E^2 \sum_{n=1}^{\infty} \frac{|\langle n | z | 0 \rangle|^2}{E_0 - E_n} .$$

(a) Suppose we had an operator  $A$  such that

$$z|0\rangle = (AH_0 - H_0A)|0\rangle , \tag{1}$$

where  $H_0$  is the unperturbed Hamiltonian for the hydrogen atom,

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r} ,$$

where  $m$  is the reduced mass of the electron and proton. Show that

$$\langle n | z | 0 \rangle = (E_0 - E_n) \langle n | A | 0 \rangle .$$

Also show that

$$\sum_{n=1}^{\infty} \frac{|\langle n | z | 0 \rangle|^2}{E_0 - E_n} = \langle 0 | zA | 0 \rangle - \langle 0 | z | 0 \rangle \langle 0 | A | 0 \rangle = \langle 0 | zA | 0 \rangle .$$

(b) So, if we knew  $A$ , we could get the answer just by calculating one matrix element. If we assume  $A$  is a function only of coordinates, then equation (1) is an inhomogeneous differential equation for  $A$ . If you're really good at differential equations, you could solve it. The result is

$$A = -\frac{ma}{\hbar^2} \left( \frac{r}{2} + a \right) z .$$

Show that this expression does, in fact, solve equation (1). (Note that the normalization of  $|0\rangle$  cancels out, so you can just take  $|0\rangle = \exp(-r/a)$ .)

- (c) Calculate the Stark effect energy shift for the ground state of hydrogen to second order in the applied field.
2. A particle in a 2D box. (Based on a problem from Merzbacher.) A particle is confined to a square box,  $0 \leq x \leq L$  and  $0 \leq y \leq L$ . We are not interested in the  $z$ -motion, so this is a 2D problem.
- (a) Obtain the energies and eigenfunctions. What is the degeneracy of the few lowest levels?
- (b) A small perturbation  $V = Cxy$ , where  $C$  is a constant, is applied. Find the energy change for the ground state and the first excited state in the lowest non-vanishing order. Construct the appropriate eigenfunctions in the case of the first excited state.
3. Hyperfine splitting of the hydrogen ground state. As you know, the spatial part of the hydrogen ground state is very simple:  $\psi_{100}(r, \theta, \phi) = \exp(-r/a) a^{(-3/2)} \pi^{(-1/2)}$ . Since there is no orbital angular momentum, there is no spin orbit effect. However, the ground state has a degeneracy of 4 since both the proton and the electron have spin 1/2. The spins can align, giving a triplet state, or anti-align, giving a singlet state. Since there are magnets associated with the spins, we expect that there should be a difference in energy between the triplet and singlet states. The nuclear spin is often denoted by  $\mathbf{I}$  and produces a magnetic moment

$$\boldsymbol{\mu}_p = \frac{eg_p}{2m_p c} \mathbf{I},$$

where  $\boldsymbol{\mu}_p$  is the magnetic moment of the proton,  $g_p$  is its  $g$ -factor and  $m_p$  is the mass of the proton. (Note: to consider other nuclei, we would use the appropriate  $Z$ ,  $g$ , and  $m$ .) We take the proton as fixed at the origin and it produces a magnetic field,

$$\mathbf{B}(\mathbf{r}) = \frac{3\mathbf{e}_r(\mathbf{e}_r \cdot \boldsymbol{\mu}_p) - \boldsymbol{\mu}_p}{r^3} + \frac{8\pi}{3} \boldsymbol{\mu}_p \delta(\mathbf{r}),$$

(Jackson, *Classical Electrodynamics*, 2nd ed., p. 184). The interaction energy of this field and the magnetic moment of the electron is

$$H_{HF} = -\boldsymbol{\mu}_e \cdot \mathbf{B} = -\frac{3(\mathbf{e}_r \cdot \boldsymbol{\mu}_e)(\mathbf{e}_r \cdot \boldsymbol{\mu}_p) - \boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p}{r^3} - \frac{8\pi}{3} (\boldsymbol{\mu}_e \cdot \boldsymbol{\mu}_p) \delta(\mathbf{r}).$$

Aside: If we were to consider other than  $s$ -states, the hyperfine Hamiltonian would also include a spin orbit term due to the interaction of the magnetic moment of the nucleus with magnetic field produced by the moving electron(s).

Evaluate the hyperfine Hamiltonian above for the ground state of hydrogen. How does it depend on the proton and electron spins? Or, what is the energy difference between the singlet and triplet states? Which is the actual ground state: triplet or singlet? What

are the wavelength and frequency of the radiation emitted or absorbed in the transition between these states? Hint: can you show that the first term in  $H_{HF}$  vanishes for  $s$ -states?

4. Zeeman splitting. We consider an atom with a single valence electron, subject to a magnetic field  $\mathbf{B} = B\mathbf{e}_z$  in the  $z$ -direction. The Hamiltonian for the electron is

$$H = H_0 + H_{so} + H_B ,$$

where

$$H_0 = \frac{P^2}{2m} + V(r) ,$$

accounts for the dominant electric interaction of the electron (for Hydrogen,  $V(r) = e^2/r$ , for alkali metals,  $V(r)$  takes account of the filled shells in an approximate way). The spin orbit interaction is

$$H_{so} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{L} \cdot \mathbf{S} = f(r) \mathbf{L} \cdot \mathbf{S} .$$

The interaction with the applied magnetic field is

$$H_B = \frac{eB}{2mc}(L_z + gS_z) = \frac{eB}{2mc}(L_z + 2S_z) = \frac{eB}{2mc}(J_z + S_z) ,$$

where the term proportional to  $B^2$  has been dropped. Also, some other small terms, for example, the relativistic correction to the momentum, have been dropped since they don't give a splitting dependent on  $j$ ,  $l$  and  $s$ . In the calculations below, we are interested in  $H_{so}$  and  $H_B$ ;  $H_0$  determines the zeroth order energies and states which are used in computing expectation values of, for example,  $f(r)$ , but can otherwise be ignored.

- (a) Suppose the magnetic field is very weak. What are the appropriate basis states and what are the spin-orbit and Zeeman splittings?
- (b) Now suppose the magnetic field is very strong so the Zeeman term is larger than the spin-orbit term. What are the appropriate states and what are the Zeeman and spin-orbit splittings?
- (c) Suppose that neither the spin-orbit nor the Zeeman effect is appreciably larger than the other. How would you determine the level splittings in this case? (This is a short essay question, no calculations are required!)

5. Virial theorem for a particle in a fixed potential. (See Schwabl, chapter 12.) Consider  $\mathbf{x} \cdot \mathbf{p}$  and a Hamiltonian  $H = p^2/2m + V(\mathbf{x})$ .

- (a) Show that

$$[H, \mathbf{x} \cdot \mathbf{p}] = -i\hbar \left( \frac{p^2}{m} - \mathbf{x} \cdot \nabla V(\mathbf{x}) \right) .$$

(b) If  $|\psi\rangle$  is a stationary state of  $H$ ,  $H|\psi\rangle = E|\psi\rangle$ , show that

$$\left\langle \psi \left| \frac{p^2}{m} \right| \psi \right\rangle - \langle \psi | \mathbf{x} \cdot \nabla V(\mathbf{x}) | \psi \rangle = 0,$$

and therefore, for the Coulomb potential,

$$2 \langle \psi | H | \psi \rangle + \left\langle \psi \left| \frac{Ze^2}{r} \right| \psi \right\rangle = 0.$$

(c) Determine  $\langle 1/r \rangle_{nl}$  for the hydrogen atom.