4 ATOMS AND RADIATION

4.1 ALLOWED AND FORBIDDEN TRANSITIONS

Transitions can occur between quantum states by SELECTION RULES. The main ones are the DIPOLE SELECTION RULES.

Definition of electric dipole moment $\underline{\boldsymbol{P}} = e\underline{r}$, can be permanent or induced. The dipole of an optically active electron interacts with electromagnetic radiation, i.e.

$$\underline{\boldsymbol{E}}(t) = \underline{\boldsymbol{E}}_0 \exp[i\omega t]$$

The Hamiltonian will have an additional term:

$$H = H_0 + V \ , \tag{1}$$

where H_0 is the unperturbed Hamiltonian and $V = -\underline{\boldsymbol{P}} \cdot \underline{\boldsymbol{E}}$ is a time-dependent perturbation, has a small effect compared to H_0.

Consider z-part of $\underline{\boldsymbol{P}} = e\underline{r}$, i.e $V_z = er\cos\theta E_{0z}\exp[i\omega t]$, ($E_{0z} =$ z component of $\underline{\boldsymbol{E}}_0$ and $z = r\cos\theta$).

From TIME-DEPENDENT PERTURBATION THEORY we can derive FERMI'S GOLDEN RULE:

Transitions occur between two quantum states $i \rightarrow f$ with a probability, T_{if}, which is given by the square of the matrix element of the perturbation:

$$\begin{aligned} T_{if} &\propto \left| \int \Psi_f^* V \Psi_i d\tau \right|^2 \\ &\propto \left| \int \Psi_f^* r\cos\theta \Psi_i d\tau \right|^2 . \end{aligned} \tag{2}$$

(Integral is independent of e and E_z, and exp . terms vanish after time integral.).

- $T_{if} = 0$ the transition is forbidden;
- $T_{if} \neq 0$ the transition is allowed.

For an atomic state of a one-electron atom, the transition $nlm \rightarrow n'l'm'$.

$$T_{if} = \underbrace{\left|\int_0^\infty R^*_{nl}(r) r R_{n'l'}(r) r^2 dr\right|^2}_{\text{radial}} \times \underbrace{\left|\int_0^{2\pi}\int_0^\pi Y^*_{lm} \cos\theta\, Y_{l'm'} \sin\theta\, d\theta d\phi\right|^2}_{\text{angular}} \quad (3)$$

Radial integral which equals some constant, C, non-zero, no selection rule.

Spherical Harmonics are orthogonal:

$$\int_0^{2\pi}\int_0^\pi Y^*_{lm}(\theta,\phi)\; Y_{l'm'}(\theta,\phi) \sin\theta\, d\theta\, d\phi = \delta_{ll'}\, \delta_{mm'}\ . \quad (4)$$

and using:

$$\cos\theta\, Y_{lm} = AY_{l+1\,m} + BY_{l-1\,m}\ , \quad (5)$$

where A and B are some constants. So

$$\int Y^*_{lm} \cos\theta\, Y_{l'm'}\, d\Omega = A\int Y^*_{lm} Y_{l'+1\,m}\, d\Omega + B\int Y^*_{lm} Y_{l'-1\,m}\, d\Omega \quad (6)$$

which, by orthogonality of the spherical harmonics, implies $l' = l \pm 1$ and $m' = m$. A similar analysis, using $x = r\sin\theta\cos\phi$ and $y = r\sin\theta\sin\phi$ gives the $\Delta m = \pm 1$ rule.

V does not depend on $\underline{\hat{S}}$, so the spin is not changed by the transition and $\Delta s = 0$.

Remember that the $V \propto \underline{r}$. Now $\underline{r}$ has **odd parity**. Integrand in T_{if} must be **even** for T_{if} to be non-zero. So product $\Psi^*_f \Psi_i$ to be **odd** and therefore both states have to be of opposite parity.

Electric dipole selection rules one-electron atom:

$\Delta l = \pm 1, \Delta m = 0, \pm 1$, $\Delta s = 0$, and states of opposite parity

Furthermore, if the spin-orbit interaction is significant then $\Delta j = 0, \pm 1$ but not $j = 0 \rightarrow j' = 0$.

Note that these are not strict selection rules. Other transitions can occur which would follow the magnetic dipole or electric quadrupole selection rules. Transition probabilities will be very small compared to those for electric dipole transitions.

See figure 4.1 and 4.2 of transitions in H and He.

4.2 EINSTEIN A AND B COEFFICIENTS

Consider the following fundamental photon-atom processes:

Spontaneous emission: Decay of an excited state to a lower state with emission of one photon energy $h\nu$ equal to energy difference between states.

Absorption: Absorption of a photon with energy $h\nu$ equal to energy difference of states between which the electron makes a transition.

Stimulated emission: A photon with energy $h\nu$ 'provokes/induces' the decay of the atom and two photons are emitted same frequency, ν, and are COHERENT, i.e., they are generated in phase.

Consider an ensemble of atoms, N_1 in a state with energy E_1 and N_2 in a state with energy, E_2. When first exposed to a thermal

radiation field of spectral energy density, $U(\nu)$, the population, N_1 and N_2 will be time-dependent.

The growth and decay of the upper and lower level populations can be expressed via the following coupled first-order differential equations

$$\frac{dN_2}{dt} = \underbrace{CU(\nu_{12})N_1}_{\text{absorption}} - \underbrace{[A + BU(\nu_{12})]N_2}_{\substack{\text{spontaneous +} \\ \text{stimulated emission}}} \tag{7}$$

$$\frac{dN_1}{dt} = [A + BU(\nu_{12})]N_2 - CU(\nu_{12})N_1 \ . \tag{8}$$

After a sufficient amount of time, equilibrium is reached and

$$\frac{dN_1}{dt} = \frac{dN_2}{dt} \rightarrow CU(\nu_{12})N_1 = [A + BU(\nu_{12})]N_2 \ . \tag{9}$$

Assuming the atoms to have a Maxwell-Boltzmann distribution gives (for a system in thermal equilibrium at temperature, T):

$$\frac{N_1}{N_2} = \frac{\exp[-E_1/kT]}{\exp[-E_2/kT]} = \exp[h\nu_{12}/kT] \ , \tag{10}$$

where $h\nu_{12} = E_2 - E_1$. So we can write

$$U(\nu_{12}) = \frac{A}{Ce^{h\nu_{12}/kT} - B} = \frac{A/B}{(C/B)e^{h\nu_{12}/kT} - 1} \ . \tag{11}$$

Comparing Eq. (11) with the spectral energy density characteristic of a black-body field (Planck's formula), i.e.,

$$U(\nu_{12}) = \frac{8\pi h\nu_{12}^3}{c^3}\frac{1}{e^{h\nu_{12}/kT} - 1} \ ;$$

Hence we can identify

$$C = B \quad \text{and} \quad A = \frac{8\pi h\nu_{12}^3}{c^3}B. \tag{12}$$

A is known as the EINSTEIN COEFFICIENT for SPONTANEOUS EMISSION.

B is the EINSTEIN COEFFICIENT for STIMULATED (INDUCED) EMISSION or ABSORPTION (we do not use C anymore).

These coefficients can be related to the transition probabilities evaluated using Fermi's Golden Rule (see Bransden and Joachain).

4.2.1 LIFETIMES

So even an isolated excited atom (i.e., without radiation to stimulate it) will spontaneously decay to a lower state with a probability

$$P_{if} = A_{if} \ , \tag{13}$$

where A_{if} is the Einstein coefficient for spontaneous emission from state i to state f.

An excited state, i, of an atom has a finite LIFETIME:

$$\Delta\tau_i = \frac{1}{\Sigma_f \, A_{if}} \sim \ 10^{-9}\,\text{s for electric-dipole transitions} \ . \tag{14}$$

By the Heisenberg uncertainty principle, there is an associated energy uncertainty:

$$\Delta\tau\Delta E \geq \hbar/2 \tag{15}$$

So, spectral lines are not perfectly sharp; even under the best experimental conditions they have an intrinsic energy width, $\Delta E \approx \frac{\hbar}{2\Delta\tau}$. Therefore if we look at the spectra we have frequency width, $\Delta\nu$, **the natural line-width** (see figure 4.3).

4.2.2 METASTABLE LEVELS

If, for a level i, spontaneous decay is forbidden by electric dipole transitions, i.e. $A_{if} = 0$ for ALL f, then the level is METASTABLE. Other possible transitions (magnetic dipole, electric quadrupole) but probability much smaller, leads to a longer lifetime.

E.g. for a 2s level in H, the transition 2s→1s by electric dipole is forbidden as $\Delta l = 0 . \Delta\tau \sim 0.14\,\mathrm{s}$ as compared to 10^{-9} s for typical electric-dipole.

4.3 LASER (Light Amplification by the Stimulated Emission of Radiation)

Consider two level system.

Boltzmann distribution: $\dfrac{N_1}{N_2} = e^{(E_2 - E_1)/kT}$, so $N_1 > N_2$ and incoming photon with energy $E = h\nu_{12}$ is more likely to be absorbed.

However, if $N_2 > N_1$, we have POPULATION INVERSION, and an incoming photon can provoke stimulated emission, two photons **phase or ' coherent'**. The two photons can go on to stimulate another 2 atoms, then 4, then 8..., etc. A cascade builds up, resulting in an intense, coherent beam of monochromatic light.

To get population inversion, we can use 3 level systems where the middle level is a metastable level.

1. The atoms are pumped from level (1) to level (3) with photons of frequency ν_{13}.
2. Atoms accumulate in level (3) which decays spontaneously down to level (2).
3. Atoms accumulate in level (2) which is metastable.
4. Levels (2) and (1) now have population inversion.
5. A beam of ν_{12} photons can result in laser light at frequency ν_{12}.

4.4 X-RAY SPECTRA OF ATOMS

So far we have been concerned with the outer, (weakly-bound) electrons which yield optical (visible), $\lambda \sim 10^{-6}$m, or uv spectra, $\lambda \sim 10^{-7} - 10^{-8}$m.

But transitions of inner electrons yield X-rays of wavelength $\lambda \sim$ 0.1–10.0 Å (10^{-9} m) corresponding to energies 1–100 keV.

They may be produced by bombarding a high Z target (anode) with energetic e^- from a heated cathode.

Types of X-ray spectra are:

1. CONTINUOUS X-rays. Fast moving electrons deflected and slowed down in the Coulomb field of heavy atoms, emits radiation giving rise to 'white' or continuous (all frequencies) radiation, known as **Bremsstrahlung radiation**.

   The electron initial and final energies, E_i and E_f, are not quantized and a continuous spectrum is seen (see figure 4.4). The limiting case occurs when an electron gives up all its

energy, i.e., $\nu_{max} = E_i/h$ or $\lambda_{min} = hc/E_i$, and this is known as absorption edge.

2. CHARACTERISTIC X-ray spectra. Transitions of inner electrons. Electron excited from an inner shell, it leaves a 'hole' which another electron from a higher state energy level can decay into by emission of an X-ray photon, characteristic of the atom and

$$\nu_{if} = \frac{E_i - E_f}{h} = RZ_{\text{eff}}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \tag{16}$$

where $Z_{\text{eff}} = Z - S$ is the effective charge and S the screening constant.

They form series (see figure 4.4):

Transitions to $n_f = 1$ are called the K-series
Transitions to $n_f = 2$ are called the L-series
Transitions to $n_f = 3$ are called the M-series

Within each series, $\Delta n (= n_i - n_f) = 1$ has subscript α, $\Delta n = 2$ has subscript β, $\Delta n = 3$ has subscript γ, etc.

So have, e.g., K_α, K_β, $K_\gamma \ldots$.

Moseley Law (empirical)

$$\sqrt{\nu_{if}} = C_n(Z - S) \tag{17}$$

where C_n is independent of Z and S is different for different series. This work led Moseley to identify Z the atomic number with the nuclear charge and enabled him to predict unknown elements (Z=43, 61, 72 and 75).

4.5 ATOMS IN EXTERNAL FIELDS

Consider the effects of **externally applied fields** (e.g., in the laboratory or a star, etc):

$$\hat{H} = \hat{H}_0(\underline{\boldsymbol{r}}_1, \underline{\boldsymbol{r}}_2, \ldots, \underline{\boldsymbol{r}}_N) + \hat{H}_{\rm SL} + V_B + V_E \ , \qquad (18)$$

where

V_B = Interaction with magnetic field (ZEEMAN EFFECT)

and

V_E = Interaction with electric field (STARK EFFECT) .

We will restrict ourselves to the perturbative case:

$$\hat{H}_0 \gg V_B, \quad V_E, \quad \hat{H}_{\rm SL}$$

so that these terms represent simply a small shift, ΔE, in the energy levels. First-order perturbation theory gives:

$$\begin{aligned} \Delta E &\simeq \int \psi^* V \psi d\tau \\ E^{\rm TOT} &= E_0 + \Delta E \end{aligned} \qquad (19)$$

where $\hat{H}_0\psi = E_0\psi$ and $E_0 \gg \Delta E$

4.6 ATOMS IN MAGNETIC FIELDS (ZEEMAN EFFECT)

Generally the perturbative limit is good: $E_0 \gg \Delta E$. For an atom in a low-lying state, $n \sim 1$ and $E_0 \sim 1$ a.u. In this case, $\Delta E \approx E_0$ for $B = 100\,000$ T. The strongest laboratory fields are of the order 10–100 T. Very strong magnetic fields are only found in, e.g., white dwarf stars. We describe the interaction using the vector-model of the atom and introduce the quantum mechanical operators when required.

4.6.1 NORMAL ZEEMAN EFFECT: $V_B \gg \hat{H}_{\rm SL}$

If $V_B \gg \hat{H}_{\rm SL}$ then $\underline{L}$ and $\underline{S}$ decouple (PASCHEN-BACK limit) and both precess independently about the $\underline{B}$-field direction (see diagram in books). The precession arises from the torque due to the $\underline{B}$-field, $\tau \propto \underline{L} \times \underline{B}$.

Therefore in this case l, s, m_l and m_s are good quantum numbers.

The potential energy arising from a magnetic moment, $\underline{\mu}_X$, is:

$$V_B = -\underline{\mu}_X \cdot \underline{B} \; . \tag{20}$$

The total the magnetic moment arises from the orbital angular momentum and the spin angular momentum, $\underline{\mu}_X = \underline{\mu}_L + \underline{\mu}_S$. We can take the z-axis to lie along the direction of $\underline{B}$ and introduce the operators in equation (20):

$$V_B = \frac{\mu_B}{\hbar} B \left(\hat{L}_z + 2\hat{S}_z \right) \; . \tag{21}$$

So that, in the case of a one-electron atom and taking ψ as being a normalised eigenfunction, we find:

$$\begin{aligned} \Delta E &= \int \psi^* \frac{\mu_B}{\hbar} B \left(\hat{L}_z + 2\hat{S}_z \right) \psi d\tau = \frac{\mu_B}{\hbar} B \int \psi^* \hbar \left(m_l + 2m_s \right) \psi d\tau \\ &= \mu_B B \left(m_l + 2m_s \right) \end{aligned} \tag{22}$$

Remember that $\mu_B = 5.788 \times 10^{-5}\,\mathrm{eV/T}$ so the effect is small.

In the case of multi-electron atom we get:

$$\Delta E = \mu_B B \left(M_L + 2M_S \right) \tag{23}$$

4.6.2 ANOMALOUS ZEEMAN EFFECT: $V_B \ll \hat{H}_{\rm SL}$

$\underline{B}$-field weak to uncouple $\underline{L}$ and $\underline{S}$ which coupled by spin-orbit interaction into $\underline{J} = \underline{L} + \underline{S}$, and both $\underline{L}$ and $\underline{S}$ precess about $\underline{J}$

which itself precesses about $\underline{B}$. Now j, l, s and m_j are good quantum numbers. (see diagrams in books)

The interaction is

$$V_B = \frac{\mu_B}{\hbar}\underline{B}\cdot(\underline{L}+2\underline{S}) = \frac{\mu_B}{\hbar}\underline{B}\cdot(\underline{J}+\underline{S}) \ . \tag{24}$$

Taking the $\underline{B}$-field along the z-axis the first part is:

$$\Delta E_A \ = \ \int \psi^* \frac{\mu_B}{\hbar} B \hat{J}_z \psi d\tau = \mu_B B m_j. \tag{25}$$

For the second part

$$\Delta E_B \ = \ \int \psi^* \frac{\mu_B}{\hbar}\underline{B}\cdot\underline{S}\psi d\tau \tag{26}$$

$\underline{S}$ precesses around $\underline{J}$ with a constant projection on $\underline{J}$ equal to S_J, other components average to zero and therefore we only need to consider the vector with length S_J in the direction of $\underline{J}$, i.e

$$\underline{S}_J = |\underline{S}_J|\hat{J} = \left(\frac{\underline{S}.\underline{J}}{J}\right)\left(\frac{\underline{J}}{J}\right) = \left(\frac{\underline{S}.\underline{J}}{J^2}\right)\underline{J}. \tag{27}$$

Now introducing the quantum mechanical operators and using the relation $\underline{\hat{J}} = \underline{\hat{L}} + \underline{\hat{S}}$ to write:

$$\underline{\hat{J}}.\underline{\hat{S}} = \frac{1}{2}[\hat{J}^2 + \hat{S}^2 - \hat{L}^2] \tag{28}$$

we get:

$$\Delta E_B \ = \ \int \psi^* \frac{\mu_B}{\hbar} B \left[\frac{\hat{J}^2 + \hat{S}^2 - \hat{L}^2}{2\hat{J}^2}\right] \hat{J}_z \psi d\tau, \tag{29}$$

which can be shown (see Brehm & Mullin or Bransden & Joachain) to be equal to

$$\Delta E_B \ = \ \mu_B B m_j \left(\frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}\right). \tag{30}$$

Adding the two contributions, the total energy shift due to the anomalous Zeeman effect is:

$$\Delta E \;=\; \mu_B B m_j g \tag{31}$$

where g is the Landé-factor given by

$$g = 1 + \left(\frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right). \tag{32}$$

For the many-electron atom case we get a similar result with

$$g = 1 + \left(\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right). \tag{33}$$

EXAMPLE: SODIUM

Consider the $3\,^2\mathrm{P}_{1/2,3/2} \rightarrow 3\,^2\mathrm{S}_{1/2}$ transition.

• If the external magnetic field is zero, $B = 0$, then we have spin-orbit coupling only. Using the spin-orbit notes, the possible values of J and energy shifts for the P levels are

$$\begin{array}{ll} J = 3/2 & \Delta E_{\mathrm{SL}}(3/2) \;= A/2 \\ J = 1/2 & \Delta E_{\mathrm{SL}}(1/2) \;= -A \end{array}$$

and then $\Delta E_{\mathrm{P}} = 3A/2$ as given by Landé Interval Rule. For S state $J = 1/2$, there is no splitting and $\Delta E_{\mathrm{S}} = 0$.

From the selection rules we find two possible transitions, $3\,^2\mathrm{P}_{3/2} \rightarrow 3\,^2\mathrm{S}_{1/2}$ and $3\,^2\mathrm{P}_{1/2} \rightarrow 3\,^2\mathrm{S}_{1/2}$, gives rise to doublet lines.

• If the external magnetic field is weak then we need to include the spin orbit interaction.

$$\Delta E \;=\; \mu_B B M_J g \tag{34}$$

and the magnetic Landé g-factor can take the following values:

$3\,^2\mathrm{S}_{1/2}$ $\quad M_J = \pm\frac{1}{2}$ and $g = 2$.

$3\,^2\mathrm{P}$ $\quad M_J = \pm\frac{1}{2}$ (for $J = \frac{1}{2}$ and $\frac{3}{2}$) giving $g = \frac{2}{3}$ and $M_J = \pm\frac{3}{2}$ (for $J = \frac{3}{2}$) giving $g = \frac{4}{3}$.

Allowed transitions have $\Delta M_J = 0, \pm 1$. This means that the two $\mathrm{P}_{3/2}$, $\mathrm{P}_{1/2} \longrightarrow \mathrm{S}_{1/2}$ D-lines in a weak magnetic field split into 10 components. Without the selection rule we would obtain 12 lines (6 upper states $\longrightarrow$ 2 lower states)

• If the external magnetic field is strong, neglect the spin orbit interaction.

$$\Delta E \;=\; \mu_B B\,(M_L + 2M_S) \tag{35}$$

For the $3\,^2\mathrm{S}$, we have M_L=0 and $M_S = \pm\frac{1}{2}$ giving $(M_L + 2M_S) = \pm 1$.

For the $3\,^2\mathrm{P}$, we have M_L= 0, ± 1 and $M_S = \pm\frac{1}{2}$ giving $(M_L + 2M_S) = \pm 2, \pm 1, 0$.

The selection rules require $\Delta M_L = 0, \pm 1$ and $\Delta M_S = 0$. This gives rise to six possible lines. However, only three are seen because pairs of the transitions have the same frequencies.

4.7 HYPERFINE STRUCTURE

Protons and neutrons are also fermions with a spin 1/2. Nuclei have a net spin, I and associated with a magnetic moment,

$\underline{\boldsymbol{\mu}}_I = g_N \mu_N \frac{\boldsymbol{I}}{\hbar}$, where μ_N is the NUCLEAR Bohr magneton which is very small: $\mu_N = \frac{m_e}{m_p}\mu_l \simeq \frac{\mu_B}{1836}$. The value taken by the g-factor, g_N, depends on the nucleus. $\underline{\boldsymbol{\mu}}_I$ produces an analogue of spin-orbit coupling with energy splittings proportional to $\underline{\boldsymbol{I}} \cdot \underline{\boldsymbol{J}}$ and $\underline{\boldsymbol{I}} \cdot \underline{\boldsymbol{S}}$. Thus, we have HYPERFINE SUB-LEVELS with total angular momentum:

$$\underline{\boldsymbol{F}} = \underline{\boldsymbol{J}} + \underline{\boldsymbol{I}} \ , \tag{36}$$

e.g., ground state of hydrogen, 1s ($j = 1/2$,$s = 1/2$ and $I = 1/2$)) has now two levels labelled F=1 and F=0. For transitions between these levels,$\Delta E = \frac{hc}{\lambda} = 0.047\,\mathrm{cm}^{-1}$ which corresponds to $\lambda = 21\,\mathrm{cm}$ (radio line used to probe interstellar hydrogen clouds).

4.8 ATOMS IN ELECTRIC FIELDS: THE STARK EFFECT

Slitting of the energy levels in a static electric field. We treat the external electric field, $\underline{E}_{ext}$, as a small perturbation

$$V_E \ll Z/r \ . \tag{37}$$

If we consider the effect of the field on two opposite charges separated by a distance r, we find that the extra small term in the Hamiltonian is:

$$V_E = -\underline{\boldsymbol{\mu}} \cdot \underline{\boldsymbol{E}}_{\mathrm{ext}} \ , \tag{38}$$

where $\underline{\boldsymbol{\mu}} = -e\underline{r}$ is the ELECTRIC DIPOLE MOMENT. If the field is taken to be along the z-axis, then

$$V_E = -(-e\underline{r}) \cdot \underline{\boldsymbol{E}}_{\mathrm{ext}} = +ezE_{\mathrm{ext}} \ . \tag{39}$$

Note: V_E is positive, i.e. repulsive and it will decrease the binding energy.

4.8.1 QUADRATIC STARK EFFECT

The Quadratic Stark Effect arises in atoms which have no intrinsic dipole moment, which is the case for most atoms. A dipole implies some charge polarization along the z-direction. E.g. an atom in an s-state:
$\Psi = R(r)Y_{00}(\theta, \phi)$. Charge distribution ($\propto |\Psi|^2$) is spherically symmetric. But, the field itself polarizes the electron distribution, inducing a dipole moment proportional to $\underline{E}_{ext}$:

$$\underline{\mu} = -\alpha \underline{E}_{ext};, \qquad \alpha = \text{polarizability of the atom} . \tag{40}$$

So the potential arising from the electric field is

$$V_E = -\underline{\mu} \cdot \underline{E}_{\text{ext}} = \alpha E_{\text{ext}}^2 \tag{41}$$

which is a term varying quadratically with the field, so will ΔE.

For the ground state of H (1s) and a field $E_{\text{ext}} \approx 10^8$ V/m we find $\Delta E \approx 2.5 \times 10^{-}6$ eV.

4.8.2 LINEAR STARK EFFECT

It occurs for atoms with an intrinsic dipole moment, $\underline{\mu}_E$, such as excited states of H and H-like atoms. For these atoms there is l-degeneracy: The eigenstates are formed from superpositions of l-orbitals, e.g. $n = 2$, $m = 0$:

$$\begin{aligned} \Psi &= R_{20}(r)Y_{00} + R_{21}(r)Y_{10} \\ &= \frac{1}{\sqrt{4\pi}} \left(R_{20}(r) + R_{21}(r)\sqrt{3}\cos\theta \right) , \end{aligned} \tag{42}$$

$$\tag{43}$$

which means that

$$|\Psi|^2 = \underbrace{a}_{\text{symmetric}} + \underbrace{b\cos\theta}_{\text{dipole}} + \underbrace{c\cos^2\theta}_{\text{symmetric}} \tag{44}$$

where a, b and c are functions of r alone. This, therefore, has a dipole so that $\Delta E \propto E_{\text{ext}}$, i.e. linear.