Physics 212b, Ken Intriligator lecture 13, Feb 28, 2018

● Hydrogen atom fine structure interactions: relativity gives $\Delta H = \sqrt{c^2 p^2 + m^2 c^4} - \frac{p^2}{2m} - mc^2 = -p^4/8m^3c^2 + \ldots$, which turns out to shift to first order by $E^{(1)}_{n,\ell,m} = -\frac{1}{2}mc^2\alpha^4(-3(4n^4)^{-1} + (n^3(\ell+\frac{1}{2}))^{-1})$. Also spin-orbit interaction, $H_{s.o.} = -\vec{\mu}\cdot\vec{B} = \frac{e^2}{2m^2c^2r^3}\vec{S}\cdot\vec{L} = \frac{e^2}{4m^2c^2r^3}(J^2 - L^2 - S^2)$. For $j = \ell + \frac{1}{2}$, $\vec{L}\cdot\vec{S} \to \hbar^2\ell/2$ and for $j = \ell - \frac{1}{2}$, $\vec{L}\cdot\vec{S} \to -\hbar^2(\ell+1)/2$. The $1/r^3$ operator is spherically symmetric and e.g. $\langle H_1 \rangle$ then involves $\int d^3\vec{r}|\psi_{n,\ell,m}(\vec{r})|^2(1/r^3)$.

Hyperfine structure and the 21 centimeter line of H: there is a magnetic dipole-dipole interaction between the proton and electron spins.

$$H_1 = \frac{|e|g_e}{2m_e c}\vec{S}_e\cdot(-\nabla\times(\frac{|e|g_p\vec{S}_p}{2M_p c}\times\nabla)\frac{1}{r}) \to \langle H_1\rangle = \frac{2}{3}\frac{e^2}{2a_0}g_p\frac{m_e}{M_p}\frac{\alpha^2}{n^3}\langle\vec{\sigma}_e\cdot\vec{\sigma}_p\rangle$$

where $\langle\vec{\sigma}_e\cdot\vec{\sigma}_p\rangle = 1$ for the triplet and -3 for the singlet. The energy difference between the two states is that of a photon with wavelength $\lambda \approx 21.106cm$. The excited state is extremely long lived (around 10 million years), hence a clean line, and it has been used since the 1950s to understand and map out hydrogen in the Universe (and the Doppler redshift of expansion).

Aside: Lamb shift of the hydrogen energy levels in QFT from interaction of the electron with the vacuum fluctuations of QFT. Superficially infinite. Once properly understood, it explains the shift between the $2S_{\frac{1}{2}}$ and $2P_{\frac{1}{2}}$ levels observed by Lamb and Retherford. Hans Bethe gave a rough estimate (based on non-relativistic QM) on the back of an envelope on a train ride. It was first properly computed in quantum electrodyamics by Normal Kroll in 1949. In 1962, Kroll was recruited to be one of the founding members of the UCSD physics department, and he was an active member of the department for 40 years.

● General atoms: $H_0 = \sum_{i=1}^Z H_{0,i}$ with $H_{0,i} = p_i^2/2m + V_c(r_i)$ where $V_c(r_i)$ is an averaged potential. $V_1 = \sum_{i<j}\frac{e^2}{|\vec{r}_i-\vec{r}_j|} - \sum_i(V_C(r_i) + \frac{Ze^2}{r_i})$. Consider example of carbon atom, i.e. $Z = 6$ electrons. Fill energy levels as $1s^2 2s^2 2p^2$. Accounting for the antisymmetry of ψ, there are $\binom{2\times 3}{2} = 15$ states, which are $^{2S+1}L = {}^3P$ (9 states), ^1S (1 state), and ^1D (5 states). These states are degenerate with H_0, and are split by V_1 according to Hund's rule: the repulsive electron-electron interaction is largest for smallest total spin (a more symmetric orbital part means the electrons have more overlap with each other) and angular momentum, so the ^1S state has the highest energy, then the ^1D. The ^3P states have the lowest energy. The spin-orbit coupling splits the degeneracy of the ^3P states, with $^3P_{J=0}$ having the lowest energy, then $^3P_{J=1}$, and finally $^3P_{J=2}$ has the highest energy.

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• Suppose a hydrogen atom is a distance R away from a charge configuration whose first non-zero multipole moment is at $\ell''' = 3$, of strength X. Which energy levels are split at leading order? Answer: the perturbation is a spherical tensor with angular momentum 3, so rotational symmetry implies that a necessary condition for a non-zero matrix element with states of angular momentum ℓ and ℓ' is that ℓ' is in the tensor product of ℓ and 3. For $n = 1, 2$, this cannot happen. For $n = 3$, rotational symmetry allows $\ell = 1$ and $\ell' = 2$ to combine into a state with $\ell'' = 3$, which is also consistent with parity.

• Example: Van Der Waals interaction. Consider two hydrogen atoms, with $\vec{r}_1$ the vector from one proton to its electron, and $\vec{r}_2$ the vector from the other proton to its electron, and $\vec{R}$ the vector from one proton to the other. The perturbation is

$$H_1 = e^2 \left(\frac{1}{R} + \frac{1}{|\vec{R} + \vec{r}_2 - \vec{r}_1|} - \frac{1}{|\vec{R} + \vec{r}_2|} - \frac{1}{|\vec{R} + \vec{r}_1|} \right) \approx \frac{e^2}{R^3} \left(\vec{r}_1 \cdot \vec{r}_2 - 3(\vec{r}_1 \cdot \hat{R})(\vec{r}_2 \cdot \hat{R}) \right)$$

Take $\vec{R} = R\hat{z}$ and then $H_1 \approx e^2(x_1 x_2 + y_1 y_2 - 2z_1 z_2)/R^3$. This is a spherical tensor with $\ell''' = 2$, so it can have non-zero matrix elements in e.g. two states with $\ell = 1$, i.e. starting at the first excited state. The first order contribution to the energy in this case leads to an energy $\sim 1/R^3$. For atoms in the groundstate there is an effect starting at second order, which leads to a potential $V_{eff}(R) \sim 1/R^6$ with negative coefficient. This is the attractive Van Der Walls interaction which e.g. explains why hydrogen atoms pair up into hydrogen molecules. Each atom polarizes the other, leading to the attractive interaction with the dipole moment operator of the second atom. Note that this is not the classical strength of an induced dipiole moment $\sim 1/R^3$, with another $\sim 1/R^3$, which would have another factor of $1/R^3$ for the interaction, leading to $1/R^9$ vs the $1/R^6$ here and observed. At short distances, need to take into account the antisymmetry of the total wavefunction and hence the exclusion principle.