.

1 Introduction

These pages **are not lecture notes**. Students are strongly encouraged to use the impressive amounts of good books on *Quantum Mechanics*.

Lectures are mostly based on

- J.J.Sakurai, Modern Quantum Mechanics
- Claude Cohen-Tannoudji, Bernard Diu, Frank Laloe, Quantum Mechanics
- Leonard Schiff, Quantum Mechanics

A previous knowledge of

- Analaytical mechanics
- Electromagnetism
- Hylbert spaces
- Schröedinger equation
- angular momentum in quantum mechanics
- unidimensional potential well and barriers
- exact solutions for the Schröedinger equation: unidimensional harmonic oscillator and hydrogen atom

is assumed.

2 Time independent perturbation theory

2.1 Non degenerate spectrum: summary

2.1.1 Notes for students

Sakurai, chapter 5.1, for introductory pourposes, previous knowledge of this subject is assumed

2.1.2 Theory summary

We have

- $$\begin{aligned} H &= H_0 + V \\ H_0 \left|n^{(0)}\right\rangle &= E_n^{(0)} \left|n^{(0)}\right\rangle \\ H \left|n\right\rangle &= E_n \left|n\right\rangle \\ E_n &= E_n^{(0)} + \Delta_n^{(1)} + \dots \\ \left|n\right\rangle &= \left|n^{(0)}\right\rangle + \left|n^{(1)}\right\rangle + \dots \end{aligned}$$

- $$\Delta_n^{(1)} = \left\langle n_0\right| V \left|n_0\right\rangle$$

- using a projector ϕ_n such that $\phi_n \left|n_{(0)}\right\rangle = 0$, $\phi_n \left|m_{(0)} \neq n_{(0)}\right\rangle = \left|m_{(0)} \neq n_{(0)}\right\rangle$, we have
$$\left|n^{(1)}\right\rangle = \frac{1}{E_n^{(0)} - H_0} \phi_n V \left|n_0\right\rangle = \sum_{k \neq n} \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}}$$

- $$\Delta_n^{(2)} = \left\langle n_0\right| V \frac{1}{E_n^{(0)} - H_0} \phi_n V \left|n_0\right\rangle = \sum_{k \neq n} \frac{|V_{kn}^2|}{E_n^{(0)} - E_k^{(0)}}$$

- $$\begin{aligned} \left|n^{(2)}\right\rangle &= \frac{1}{E_n^{(0)} - H_0} \phi_n (V - \Delta_n^{(1)}) \frac{1}{E_n^{(0)} - H_0} \phi_n V \left|n_0\right\rangle \\ &= \frac{1}{E_n^{(0)} - H_0} \phi_n V \frac{1}{E_n^{(0)} - H_0} \phi_n V \left|n_0\right\rangle - \left\langle n_0\right| V \left|n_0\right\rangle \frac{1}{E_n^{(0)} - H_0} \phi_n \frac{1}{E_n^{(0)} - H_0} \phi_n V \left|n_0\right\rangle \\ &= \sum_{k \neq n, m \neq n} \frac{V_{mk} V_{kn}}{\left(E_n^{(0)} - E_k^{(0)}\right)\left(E_k^{(0)} - E_m^{(0)}\right)} \left|m_0\right\rangle + \sum_{k \neq n} \frac{V_{nn} V_{kn}}{\left(E_n^{(0)} - E_k^{(0)}\right)^2} \left|k_0\right\rangle \end{aligned}$$

- *Notice that the perturbative correction always appear as*
$$\frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}}$$
thus a criterion to judge about the reliability of the approximation is the smallness of the above ratio

- Notice that perturbative expansion, however, cannot catch non perturbative axpect of the theory. The potential $V = \omega x^2 + g x^3$ doesn't admit bound states. Treating g as a small quantity yields an harmonic oscillator spectrum with no unbound state. It sill remain a useful approximation for quasi stable states.

- Suggested exercize: diagonalize exactly the hamiltonian

$$H = \begin{pmatrix} 3+\epsilon & 2\epsilon \\ 2\epsilon & 1-2\epsilon \end{pmatrix}$$

  Find eigenvector and eigenvalues. Check that first order perturbation theory does indeed provide first order expansion in ϵ of the exact results

2.2 Time independent perturbation theory: degenerate case

2.2.1 Notes for students

Sakurai, chapter 5.2

The student is assumed to know the *prescription* to deal with this case, *no demonstration is required*. The student is *assumed* to *know* how to deal with perturbation theory in the non degenerate case, to discuss a few relevant examples, and be aware of the limitation of the provided prescription.

2.2.2 Sketch of the lectures

If the unperturbed hamiltonian has degenerate states the above formulas cannot be applied.

The procedure must be modified as follows

- For a degenerate level the above formulas cannot be applied: denominators vanish for equal energies (notice also that there is an ambiguity in defining zeroth order eigenkets)

- Diagonalize the perturbation into the degenerate subspaces. In this way one obtains first order energy corrections and zeroth order eigenket.

- Apply ordinary non degenerate perturbation theory formulas. Now the projection operator ψ_n project out the degenerate subspace.

$$\phi_n = \sum_{j, E_j^{(0)} \neq E_n^{(0)}} |n_j\rangle \langle n_j| ; \quad H_0 \left|n_j^{(0)}\right\rangle = E_n^{(0)} \left|n_j^{(0)}\right\rangle$$

- Example:

$$\begin{aligned} H_0 &= \begin{pmatrix} E_1 & 0 & 0 \\ 0 & E_1 & 0 \\ 0 & 0 & E_2 \end{pmatrix} \\ V &= \lambda \begin{pmatrix} V_{11} & V_{12} & V_{13} \\ V_{12}^* & V_{22} & V_{23} \\ V_{13}^* & V_{23}^* & V_{33} \end{pmatrix} \end{aligned}$$

We first diagonalize V restricted to the degenerate subspace

$$\tilde{V} = \lambda \begin{pmatrix} V_{11} & V_{12} \\ V_{12}^* & V_{22} \end{pmatrix}$$

we have

$$\begin{aligned} \tilde{V}' &= \lambda \begin{pmatrix} \frac{V_{11}+V_{22}}{2} + \sqrt{\frac{(V_{11}-V_{22})^2}{4} + |V_{12}|^2} & 0 \\ 0 & \frac{V_{11}+V_{22}}{2} - \sqrt{\frac{(V_{11}-V_{22})^2}{4} + |V_{12}|^2} \end{pmatrix} \\ |1'\rangle &= \cos\alpha\, |1\rangle + \mathrm{e}^{i\beta} \sin\alpha\, |2\rangle \\ |2'\rangle &= \cos\alpha\, |2\rangle - \mathrm{e}^{-i\beta} \sin\alpha\, |1\rangle \end{aligned}$$

- in the new basis

$$\begin{aligned} H_0' &= H_0 \\ V' &= \lambda \begin{pmatrix} V_+ & 0 & V_{13}' \\ 0 & V_- & V_{23}' \\ V_{13}'^* & V_{23}'^* & V_{33} \end{pmatrix} \end{aligned}$$

where

$$\begin{aligned} V_\pm &= \frac{V_{11}+V_{22}}{2} \pm \sqrt{\frac{(V_{11}-V_{22})^2}{4} + |V_{23}|^2} \\ V_{13}' &= \cos\alpha V_{13} + \mathrm{e}^{-i\beta} \sin\alpha V_{23} \\ V_{23}' &= \cos\alpha V_{23} - \mathrm{e}^{i\beta} \sin\alpha V_{13} \end{aligned}$$

- we are now in the position to perform the standard perturbative expansion

$$\begin{aligned}
\mathcal{E}_1 &= E_1 + \lambda V'_{11} + \lambda^2 \frac{|V'_{13}|^2}{E_1 - E_2} \\
\mathcal{E}_2 &= E_1 + \lambda V'_{22} + \lambda^2 \frac{|V'_{23}|^2}{E_1 - E_2} \\
\mathcal{E}_3 &= E_2 + \lambda V'_{33} + \lambda^2 \frac{|V'_{13}|^2 + |V'_{23}|^2}{E_2 - E_1} \\
|\psi_1\rangle &= |1'\rangle + \lambda \frac{V'_{13}}{E_1 - E_2} |3'\rangle \\
|\psi_2\rangle &= |2'\rangle + \lambda \frac{V'_{23}}{E_1 - E_2} |3'\rangle \\
|\psi_3\rangle &= |3'\rangle + \lambda \frac{V'_{31}}{E_2 - E_1} |1'\rangle + \lambda \frac{V'_{32}}{E_2 - E_1} |2'\rangle
\end{aligned}$$

- suggested exercize: diagonalize exactly the hamiltonian

$$H = \begin{pmatrix} \epsilon & \epsilon & 2\epsilon \\ \epsilon & \epsilon & 2\epsilon \\ 2\epsilon & 2\epsilon & 1 \end{pmatrix}$$

  and find eigenvector end eigenvalues (notice that H has manifestly zero determinant). Check that first order perturbation theory, degenerate case, does indeed provide first order expansion in ϵ of the exact results.

3 Invariance under rotations, the Wigner-Eckart theorem

3.1 Notes for student

Lectures follow Sakurai chapter 3.11

The student is assumed to know the definition of tensor operators (both cartesian and spherical) and to be able to cope with specific relevant examples. The student is assumed to have a detailed operative knowledge of the

Wigner-Eckart theorem. No demonstration is required. The student should know how to use the theorem and to be able to discuss a few relevant phenomenological application. Rules are provided to move from cartesian to spherical tensor, again no detailed demonstration is required only a good understunding of how to obtain the relevant realtionships.

3.2 Introduction

Newton equation are *covariant* under rotations. Namely the equations are invariant in form under the action of a rotations.

These implies, in classical mechanics, that

- we have conserved quantities, angular momentum
- comparing the motion in different reference frames we don't need to solve the equations again
- each relevant physical quantity will have definite transformation rules under the action of a rotation.

  The relationships among different frames will be of purely geometric nature and to move from one frame to another we don't need to solve the dynamical problem again.

We expect something similar to happen in QM. The formal expression of rotational invariance in QM context is the *Wigner-Eckart theorem*

3.3 Examples

Let $|\alpha\rangle$ be the state vector of a two level spin 1/2 system. Let's consider the expectation value of S_x.

$$\langle +| S_x |+\rangle = \langle -| S_x |-\rangle = 0; \qquad \langle +| S_x |-\rangle = \langle -| S_x |+\rangle = \frac{1}{2}$$

Let's operate a $\pi/2$ rotation around the z axis. We have

$$|\pm\rangle \to |\pm'\rangle = \mathrm{e}^{\mp i\pi/4} |\pm\rangle$$

and thus

$$\begin{aligned} \langle +| S_x |-\rangle &\to \langle +'| S_x |-'\rangle = i = -\langle +| S_y |-\rangle \\ \langle -| S_x |+\rangle &\to \langle +'| S_x |-'\rangle = -i = -\langle +| S_y |-\rangle \\ S_x &\to S_y \end{aligned}$$

Rotating the state vector is equivalent to rotate the operator (with the state vector unchanged). In more generality we say that the set

$$\mathbf{S} = \{S_x, S_y.S_z\}$$

is a *vectorial operator* namely under the action of a frame rotation its *matrix elements* do transform like

$$\langle\psi_j| S_k |\phi_{j'}\rangle \xrightarrow{R} \langle\psi_j| (\mathcal{D}^J)^\dagger(R) S_k \mathcal{D}^{J'}(R) |\phi_{j'}\rangle = (R^{-1})_{kl} \langle\psi|_j S_l |\phi_{j'}\rangle$$

where $|\psi_j\rangle$ and $|\phi_{j'}\rangle$ are eigenkets of the J^2 operator with quantum number j and j' respectively. Therefore $\mathbf{S}$ can be regarded as a vector in the above sense: *the action of a rotation can be thought as acting on the operator itself whose matrix elements transform as if the operator is rotated with the state ket unchanged*

This property of the S_j operators allows us *to deduce geometrical relationships among its expectation values between J^2 eigenkets* Back to our example, performing a rotation around the x axis we can deduce $\langle -| S_x |-\rangle$ from $\langle +| S_x |+\rangle$. Indeed under a rotation around the x axis a spinor transform as

$$\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} \to \begin{pmatrix}\psi_1'\\ \psi_2'\end{pmatrix} = \mathrm{e}^{-i\alpha S_x}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix} = \begin{pmatrix}\cos\frac{\alpha}{2} & -i\sin\frac{\alpha}{2}\\ -i\sin\frac{\alpha}{2} & \cos\frac{\alpha}{2}\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}$$

choosing $\alpha = \pi$ and recalling the *definition* of a vectorial operator we obtain

$$\langle -| S_x |-\rangle = \langle +| S_x |+\rangle$$

Thus by knowing just a few expectation values of an arbitray component S_j we can deduce the expectation values of all S_k on an arbitrary state vector. This is a particular case of the Wigner-Eckart theorem.

3.4 Tensorial Operators

- Let $|\alpha\rangle$ be a state vector and assume it trasforms as an irreducible representation under rotation

  $$|\alpha_j\rangle \xrightarrow{R} \mathcal{D}^{(J)}(R) |\alpha_j\rangle$$

  Let V be an operator acting on $|\alpha_j\rangle$. The expectation value of V, under a rotation, changes as follows

  $$\langle\alpha_j| V |\beta_{j'}\rangle \xrightarrow{R} \langle\alpha_j| \mathcal{D}^\dagger(R) V \mathcal{D}(R) |\beta_{j'}\rangle$$

If a for set of operators V_k

$$\langle\alpha_j|\, V_k\, |\beta_{j'}\rangle \stackrel{R}{\to} \langle\alpha_j|\, \mathcal{D}^\dagger(R) V_k \mathcal{D}(R) |\beta\rangle_{j'} = R^{-1}_{kl}\, \langle\alpha_j|\, V_l\, |\beta_{j'}\rangle$$

where R is the usual 3×3 rotation matrix we say that the operator V_j is a *vectorial operator*. Specifying R to be, for example, an infinitesimal rotation around the z axis

$$\begin{aligned} \mathcal{D}(R) &= \mathbf{1} - i\epsilon J_z \\ R &= \begin{pmatrix} 1 & \epsilon & 0 \\ -\epsilon & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{aligned}$$

we can explicitly show that V_j satisfy $(\langle\alpha|\, \{\mathbf{1} + i\epsilon[J_z, V_j]\}\, |\alpha\rangle = [\delta_{jk} - i\epsilon J_{zjk}]\, \langle\alpha|\, V_k\, |\alpha\rangle)$ the commutation relation

$$[V_j, J_k] = i\epsilon_{jkl} V_l$$

which implies

$$V_j \stackrel{R}{\to} \mathbf{e}^{i\mathbf{J}\phi} V_j \mathbf{e}^{-i\mathbf{J}\phi}$$

- In a completely analogous manner we define a tensorial operator $V_{j_1 j_2 \ldots j_n}$ as a set of operators transforming as

$$V_{j_1 j_2 \ldots j_n} \stackrel{R}{\to} R_{j_1 k_1} R_{j_2 k_2} \ldots R_{j_n k_n} V_{k_1 k_2 \ldots k_n}$$

  $V_{j_1 j_2 \ldots j_n}$ is usually referred to as a Cartesian tensor and transforms as a *reducible* representation of the rotation group.

- A more convenient set of operators is a *spherical tensor* namely a set $T^{(k)}_q$ transforming as

$$T^{(k)}_q \stackrel{R}{\to} \mathcal{D}^{(k)}_{qq'} T^{(k)}_{q'}$$

  i.e. exactly the same transformation law of spherical armonics. An alternative definition of a spherical tensor is via its commutation relation with the angular momentum generators

$$\begin{aligned} [J_z, T^{(k)}_q] &= q T^{(k)}_q \\ \left[J_\pm, T^{(k)}_q\right] &= \sqrt{(k \mp q)(k \pm q + 1)}\, T^{(k)}_{q\pm 1} \end{aligned}$$

- The way to combine two spherical tensor $T_q^{(k_1)}$ and $T_q^{(k_2)}$ to obtain a tensor $T_q^{(k)}$ is

$$T_q^{(k)} = \sum_{q_1} \sum_{q_2} \langle k_1 k_2; q_1 q_2 |\, k_1 k_2; kq \rangle T_{q_1}^{(k_1)} T_{q_2}^{(k_2)} \tag{1}$$

  where $\langle k_1 k_2; q_1 q_2|$ are the *Clebsch-Gordan coefficient* for the addition of two angular momenta k_1 and k_2 to obtain an angular momenta k.

3.5 Wigner-Eckart theorem

- The matrix element of tensorial operators among angular momentum eigenstates satisfy the relation

$$\langle \alpha', j', m' |\, T_q^{(k)} \,| \alpha, j, m \rangle = \frac{\langle j, k; mq |\, j, k; j'm' \rangle}{\sqrt{2j+1}} \langle \alpha', j' |\, |T_q^{(k)}|\, | \alpha, j \rangle$$

  where the matrix element $\langle |\, |T_q^{(k)}|\, | \rangle$ is independent from m and m' and depends only from j, j' and the dynamics of the system (α). *Notice that in the above formula $|j, m\rangle$ are angular momentum eigenstates and $T_q^{(k)}$ spherical tensor.* Using different representations the theorem still holds but the coefficients are changed. Since the Clebsch-Gordan coefficient are tabulated it is more convenient to transform first to angular momentum eigenstates and spherical tensor and then apply the theorem.

- selection rules

$$\begin{aligned} |j-k| &\leq j' \leq j+k \\ m' &= q+m \end{aligned}$$

- scalar operator: only matrix element among states with the same j and m can be non zero

- vectorial operator: selection rules

$$\begin{aligned} \Delta m &= 0, \pm 1 \\ \Delta j &= 0, \pm 1 \end{aligned}$$

morover the transition $j ==\!\!\rightarrow j' = 0$ is forbidden. If $j = j'$ we have

$$\langle \alpha', j, m' | \, V_q \, | \alpha, j, m \rangle = \frac{\langle \alpha', j, m | \, \mathbf{JV} \, | \alpha, j, m \rangle}{j(j+1)} \, \langle j, m' | \, | J_q | \, | jm \rangle$$

known also as *projection theorem.*

Let's now establish the connection between cartesian and spherical operators. For the coordinates

$$\langle \psi | \, r_j \, | \psi' \rangle \stackrel{R}{\rightarrow} R_{jk} \, \langle \psi | \, r_k \, | \psi' \rangle$$

thus the coordinate operators are a cartesian vector.

From r_j we can *build a rank 1 spherical tensor*

$$\begin{aligned} [J_z, z] &= 0 \Rightarrow T^1_0 = z \\ [J_+, z] &= -x - iy \Rightarrow T^1_1 = \frac{1}{\sqrt{2}}(-x - iy) \\ [J_-, z] &= x - iy \Rightarrow T^1_{-1} = \frac{1}{\sqrt{2}}(x - iy) \end{aligned} \tag{2}$$

the generalization to a generic vector operator V_j is straightforward, just trade $r_j \rightarrow V_j$

Notice that, up to an overall constant T^1 "is" the rank 1 spherical armonic. (To be more accurate the spherical armonics are built up from the eigenvalues of the coordinate operators ane therefore the correspondence is between operator and its eigenvalues) This is understood since spherical harmonics are built from the eigenvalues of the position operator and the commutation relationships for a spherical tensor match the transformation laws of spherical harmonics under rotations.

Let's now consider a rank two cartesian tensor and its decomposition into spherical tensor. We are interested only into its properties under a rotation. Thus we can write a rank two tensor as a direct product of two rank one tensors.

$$\tau_{ij} = a_i b_j$$

where both $\mathbf{a}$ and $\mathbf{b}$ are vectors. As a product of two rank one tensors τ will be decomposed into the direct sum of rank zero, one and two spherical tensor.

We have

$$T^0 \sim \mathbf{ab} \tag{3}$$

$$\begin{aligned} T_1 &\sim \begin{pmatrix} -c_x - ic_y \\ \sqrt{2}z \\ c_x - ic_y \end{pmatrix} \\ \mathbf{c} &= \mathbf{a} \times \mathbf{b} \end{aligned}$$

$$T^2 = \begin{pmatrix} a_x b_x + i a_x b_y + i a_y b_x - a_y b_y \\ -a_z(b_x + i b_y) - b_z(a_x + i a_y) \\ \frac{1}{\sqrt{6}}(-2a_x b_x - 2a_y b_y + 4a_z b_z) \\ a_z(b_x - i b_y) + b_z(a_x - i a_y) \\ a_x b_x - i a_x b_y - b_y b_y \end{pmatrix} \tag{4}$$

The student is invited to check that the above espression do indeed fullfill the definition of the corresponding spherical tensor. Use momentum and spin as $\mathbf{a}$ and $\mathbf{b}$.

A list of a few possible ways to obtain the above relationships

- the most straightforward way is to use the definition of a spherical tensor:
  1. start from any component and compute $[J_+, \tau_{ij}]$ continue until you obtain zero.
  2. once you obtain $[J_+, \tilde{\tau}] = 0$ then $\tilde{\tau}$ acting with J_- you obtain the full rank k tensor ($k = 0, 1, 2$ depending on the τ_{lm} chosen to start)
  3. Choose another $\tau_{l'm'}$ remove its component along the previously found tensors and repeat until you find the three tensors.
- a bit more efficent (and slightly less straightforward):
  1. use eq. 2 to build two spherical tensor T^1_j and R^1_j out of the two cartesian vector $\mathbf{a}$ and $\mathbf{b}$
  2. use the addition rule of eq. 1 to obtain three sperical tensors of rank zero one and two respectively
- finally less straightforward but much quicker, use the correspondence between spherical harmonics and spherical tensors built out of combination of polinomials in the coordinate operators:

1. out of the product of two cartesian vectors it is straightforward to build combinations with specific properties under rotations

$$\mathbf{ab}; \quad \mathbf{a}\times\mathbf{b}; \quad a_j b_k + a_k b_j - \frac{2}{3}(\mathbf{ab})\delta_{jk}$$

which are a scalar, a vector and a symmetric traceless rank two tensor. These combination do correspond to rank zero one and two respectively. The scalar is trivial and is mapped into rank zero spherical tensor. For the vector we already know the mapping from cartesian to spherical. For the rank two we can use as the special set of $\mathbf{a} = \mathbf{b} = \mathbf{r}$ cartesian operators. The combination which give rise to the rank two tensor can be read directly from the expression of the rank two spherical harmonics as a function of r_j. The generalization to two *distinct* operators $\mathbf{a}$ and $\mathbf{b}$ is obtained ensuring that it is symmetric under the exchange of $\mathbf{a}$ and $\mathbf{b}$

Add some comments and references to group theory, in particular group representations

3.6 Examples

- Let's consider for example

$$\langle \alpha, 2, m |\, z \,| \alpha', 1, m' \rangle = \int \mathrm{d}\rho\ \rho^2 f^{(2)}_{\alpha'}(\rho) f^{(1)}_{\alpha}(\rho) \rho \int \mathrm{d}\Omega Y_2^m Y_1^{m'} \cos\theta$$

Where

$$\begin{aligned}
Y_2^2 &= \frac{1}{4}\sqrt{\frac{15}{2\pi}}\mathrm{e}^{2i\varphi}\sin^2\theta = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\frac{(x+iy)^2}{r^2} \\
Y_2^1 &= -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\mathrm{e}^{i\varphi}\sin\theta\cos\theta = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\frac{(x+iy)z}{r^2} \\
Y_2^0 &= \frac{1}{4}\sqrt{\frac{5}{2\pi}}(3\cos^2\theta - 1) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\frac{2z^2 - x^2 - y^2}{r^2} \\
Y_2^{-1} &= \frac{1}{2}\sqrt{\frac{15}{2\pi}}\mathrm{e}^{-i\varphi}\sin\theta\cos\theta = \frac{1}{2}\sqrt{\frac{15}{2\pi}}\frac{(x-iy)z}{r^2} \\
Y_2^{-2} &= \frac{1}{4}\sqrt{\frac{15}{2\pi}}\mathrm{e}^{-2i\varphi}\sin^2\theta = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\frac{(x-iy)^2}{r^2}
\end{aligned}$$

The required matrix element is then factorized as a factor which doesn't depend on m times an m dependent factor. The ratio among m dependent factors is entirely specified in terms of the appropriate Clebsch-Gordan coefficients. We have the freedom to choose what way to apply the Wigner-Eckart theorem. In order to simplify the calculation we choose to "add" two $j = 1$ representations to obtain a $j = 2$ representation. We recall that

$$\begin{aligned}
|j_1 = 1, j_2 = 1; j = 2, j_z = \pm 2\rangle &= |j_1 = 1, j_2 = 1; j_{1z} = \pm 1, j_{2z} = \pm 1\rangle \\
|j_1 = 1, j_2 = 1; j = 2, j_z = \pm 1\rangle &= \frac{1}{\sqrt{2}} \left(|j_1 = 1, j_2 = 1; j_{1z} = \pm 1, j_{2z} = 0\rangle \right. \\
&\quad \left. + |j_1 = 1, j_2 = 1; j_{1z} = 0, j_{2z} = \pm 1\rangle\right) \\
|j_1 = 1, j_2 = 1; j = 2, j_z = 0\rangle &= \frac{1}{\sqrt{6}} \left(|j_1 = 1, j_2 = 1; j_{1z} = 1, j_{2z} = -1\rangle \right. \\
&\quad + |j_1 = 1, j_2 = 1; j_{1z} = -1, j_{2z} = 1\rangle + \\
&\quad \left. 2\,|j_1 = 1, j_2 = 1; j_{1z} = 0, j_{2z} = 0\rangle\right)
\end{aligned}$$

Let's denote by

$$\begin{aligned}
\mathcal{C}^{z}_{mm'} &= \langle 2, m| \frac{z}{\rho} |1, m'\rangle \\
\mathcal{C}^{\pm}_{mm'} &= \frac{1}{\sqrt{2}} \langle 2, m| \frac{x \mp iy}{\rho} |1, m'\rangle
\end{aligned}$$

according to the Wigner-Eckart theorem we have

$$\begin{aligned}
\mathcal{C}^z_{\pm 1\pm 1} &= \frac{1}{\sqrt{2}}\mathcal{C}_0 \\
\mathcal{C}^z_{00} &= \sqrt{\frac{2}{3}}\mathcal{C}_0 \\
\mathcal{C}^+_{21} &= \mathcal{C}_0 \\
\mathcal{C}^+_{10} &= \frac{1}{\sqrt{2}}\mathcal{C}_0 \\
\mathcal{C}^+_{0-1} &= \frac{1}{\sqrt{6}}\mathcal{C}_0 \\
\mathcal{C}^-_{-2-1} &= \mathcal{C}_0 \\
\mathcal{C}^-_{-10} &= \frac{1}{\sqrt{2}}\mathcal{C}_0 \\
\mathcal{C}^-_{01} &= \frac{1}{\sqrt{6}}\mathcal{C}_0
\end{aligned}$$

with all other entries zero. For $\mathcal{C}_0$ we have

$$\mathcal{C}_0 = \sqrt{\frac{3}{2}}\int \mathrm{d}\Omega\ Y_2^0 Y_1^0 c_\theta = \frac{\sqrt{1}5}{4}\sqrt{\frac{3}{2}}\int \mathrm{d}c_\theta\ \left(3c_\theta^4 - c_\theta^2\right) = \frac{3\sqrt{5}}{4\sqrt{2}}\frac{8}{15} = \sqrt{\frac{2}{5}}$$

Let's cross check a few others value

$$\begin{aligned}
\mathcal{C}^z_{11} &= \int \mathrm{d}\Omega\ (Y_2^1)^* Y_1^1 c_\theta = \frac{3\sqrt{5}}{4}\int \mathrm{d}c_\theta\ c_\theta^2(1-c_\theta^2) = \frac{3\sqrt{5}}{4}\frac{4}{15} = \sqrt{\frac{1}{5}} \\
\mathcal{C}^+_{10} &= \frac{1}{\sqrt{2}}\int \mathrm{d}\Omega\ (Y_2^1)^* Y_1^0 s_\theta \mathrm{e}^{-i\phi} = \frac{1}{\sqrt{2}}\frac{3}{2}\sqrt{\frac{5}{2}}\int \mathrm{d}c_\theta\ c_\theta^2(1-c_\theta^2) = \frac{3\sqrt{5}}{4}\frac{4}{15} = \sqrt{\frac{1}{5}} \\
\mathcal{C}^+_{0-1} &= \frac{1}{\sqrt{2}}\int \mathrm{d}\Omega\ (Y_2^0)^* Y_1^{-1} s_\theta \mathrm{e}^{-i\phi} = -\frac{1}{\sqrt{2}}\frac{\sqrt{15}}{4\sqrt{2}}\int \mathrm{d}c_\theta\ (3c_\theta^2-1)(1-c_\theta^2) \\
&= -\frac{\sqrt{15}}{8}\left(-2+\frac{8}{3}-\frac{6}{5}\right) = \frac{\sqrt{15}}{4}\frac{8}{15} = \frac{1}{\sqrt{15}}
\end{aligned}$$

Notice that it is crucial that we operate with $x \pm iy$ and not x and y, the Wigner-Eckart theorem applies to spherical tensors

4 Discrete Simmetries: Parity

4.1 Notes for Students

Sakurai chapter 4

4.2 The parity operator

Let's consider the operation of space reversal

$$\mathbf{x} \to -\mathbf{x}$$

At the quantum mechanical level the transformation will be operated by an operator π called the *PARITY*, $\mathcal{P}$ operator. The action of the $\mathcal{P}$ operator on a state vector is

$$|\alpha\rangle \xrightarrow{\mathcal{P}} \pi\,|\alpha\rangle$$

we require that π inverts the expectation value of the coordinate operator,

$$\langle\alpha|\,\pi^\dagger \hat{\mathbf{x}} \pi\,|\alpha\rangle = -\,\langle\alpha|\,\mathbf{x}\,|\alpha\rangle$$

which implies

$$\pi\hat{\mathbf{x}} - \hat{\mathbf{x}}\pi = 0$$

from which we obtain

$$\hat{\mathbf{x}}\pi\,|\mathbf{x}\rangle = -\pi\hat{\mathbf{x}}\,|\mathbf{x}\rangle = -\mathbf{x}\pi\,|\mathbf{x}\rangle$$

namely $\pi\,|\mathbf{x}\rangle$ is an eigenstate of the coordinate operator with reversed eigenvalue

$$\pi\,|\mathbf{x}\rangle = \mathrm{e}^{i\delta}\,|-\mathbf{x}\rangle$$

The phase δ is arbitrary and physically unobservable and thus it is usually set to 1. With this choice, observing that acting twice with the parity operator on a state ket one goes back to the original state, the parity operator has two eigenvalues ± 1. They correspond to even and odd wavefunctions.

- $$\hat{\mathbf{p}}\pi + \pi\hat{\mathbf{p}} = 0 \tag{5}$$

  This can be expected of the analogy with classical mechanics $p = \mathrm{d}x/\mathrm{d}t$ which reverses sign under coordinate reversal or more selfconsistently

remebering that $\hat{\mathbf{x}}$ is the generator of spatial translations. A spatial translation, followed by coordinate reversal is equivalent to *minus* coordinate reversal followed by the same translation. At the operator level

$$\pi^\dagger \left(\mathbf{1} + i\epsilon\hat{\mathbf{p}}\delta\right)\pi = \left(\mathbf{1} - i\epsilon\hat{\mathbf{p}}\delta\right)$$

which implies (11). *Notice that parity and momentum anticommute and thus momentum eigenstates are not necessarily parity eigenstate; for example plane waves are not parity invariant.*

- Again in analogy with the classical analogue we can infer that angular momentum *commute* with parity operators. This can be seen esplicitly for orbital angular momentum $\hat{\mathbf{L}} = i\hat{\mathbf{x}} \times \hat{\mathbf{p}}$ and using anticommutation relations for coordinate and momentum operators. For a generic spin J representation the property can be inferred looking at the action of parity and angular momentum on the fundamental representation. The commutation relation $[J_m, \pi] = 0$ is then inherited by arbitrary representations. [1] *The angular momentum operator* $\hat{\mathbf{J}}$ *is an example of pseudo-vector. The scalar operator* $\hat{\mathbf{x}}\hat{\mathbf{J}}$ *which changes sign under parity is an example of pseudo-scalar.*

- Since parity and angular momentum commute, angular momentum eigenstates are parity eigenstates. It can be shown that, under parity

$$\pi \left|l, m\right\rangle = (-1)^l \left|l, m\right\rangle$$

This can be shown by considering explictly the form of spherical armonics and the action of coordinate reversal. Alternatively taking into account that J_l and π commute one can consider olny the action of parity on the $|l, 0\rangle$ states or one can take into account that

$$\langle 1, m| \equiv \left(\frac{x + iy}{\sqrt{2}}, z, \frac{x - iy}{\sqrt{2}}\right)$$

which is therefore of parity -1. The spherical armonic of order l can be obtained composing l times the $l = 1$ states and therefore to odd l will corrispond odd parity and to even ones even parity.

[1] For the fundamental representation $P = -I$ and commute with an arbitrary rotation R. If we seek a representation of the group of proper rotation and time inversion a generic representation is such that $\mathcal{D}(R)\mathcal{D}(P) = \mathcal{D}(RP) = \mathcal{D}(PR)$

- Notice that if parity commute with the hamiltonian than *non degenerate* hamiltonian eigenstates are parity eigenstates. This follows for example from the fact that two operators that commute can be simultaneously diagonalized.

    1. Consider one dimensional harmonic oscillator. The Hamiltonian is invariant under parity, all the eigenvalues are non degenerate and thus all the eigenstates are also parity eigenstates (parity $(-1)^n$).
    2. Consider a free particle. Plane wave solutions *are not* parity eigenstate. This is due to the twofold degeneracy of the state ket: both $|\mathbf{p}\rangle$ and $|-\mathbf{p}\rangle$ are hamiltonian eigenstates with the same energy. It is obviously possible to construct superpositions which are also parity eigenstates $|\mathbf{p}\rangle \pm |-\mathbf{p}\rangle$ (they are not momentum eigenstate, momentum and parity don't commute and cannot be simultaneously diagonalized).

4.3 Parity selection rule

If an operator has definite properties under parity transformation it can connect only states with specific parities. The operator $\mathbf{r}$ connects only states of opposite parity.

$$\langle \alpha | \, \mathbf{r} \, | \beta \rangle \neq 0$$

only if $P_\alpha P_\beta = -1$ Equivalently one can observe that $\int \psi_\alpha(\mathbf{r}) \mathbf{r} \psi_\beta(\mathbf{r})$ is equal to zero if both wave function are (anti-)symmetric. It follows that for non degenerate eigenstates of the Hamiltonian $|n\rangle$

$$\langle n | \, \mathbf{r} \, | n \rangle = 0$$

which in turns implies that these states have vanishing *electric dipole moment*.

The above argument can be generalized to any operator of given parity. A scalar operator, like $\mathbf{J_1 J_2}$ for example, can connect only states with the same parity, whereas a pseudoscalar operator ($\mathbf{J_1 \hat{p}}$) can connect only states of opposite parity.

5 Interaction of a charged particle with an Electromagnetic Field

5.1 Notes for students

Cohen, appendix III; Cohen, complement H_{III} Sakurai, chapter 2.7

5.2 Hamiltonian for a charged particle into an Electromagnetic Field

See Cohen, appendix III for example. The student is required to know the general form of the hamiltonian in presence of an external electro-magnetic field and its specific form in the cases of interest.

Let's recall the interaction of a classical particle with an Electromagnetic Field

$$\begin{aligned} \mathcal{S} &= \int \mathcal{L} = \int \frac{1}{2m}\dot{\mathbf{r}}\dot{\mathbf{r}} + \frac{\mathrm{q}}{c}\dot{\mathbf{r}}\mathbf{A} - \mathrm{q}\Phi \\ \mathcal{H} &= \int \mathbf{p}\dot{\mathbf{r}} - \mathcal{L} = \int \frac{1}{2m}(\mathbf{p} - \frac{\mathrm{q}}{c}\mathbf{A})^2 + \mathrm{q}\Phi \end{aligned}$$

The quantization of the system proceeds promoting $\mathbf{p}$ to momentum operator. The quantum Hamiltonian is

$$H = \frac{1}{2}\left(\hat{\mathbf{p}}\hat{\mathbf{p}} - \mathrm{q}\hat{\mathbf{p}}\mathbf{A} - \mathrm{q}\mathbf{A}\hat{\mathbf{p}} - \mathrm{q}^2A^2\right) + \mathrm{q}\Phi$$

Notice that $\hat{\mathbf{p}}$ *and* $\mathbf{A}$ *don't commute. The above expression is therefore a priori ambiguos. The ambiguity is removed requiring that the hamiltonian is hermitian. One could make* $\hat{\mathbf{p}}\mathbf{A} = \mathbf{A}\hat{\mathbf{p}}$ *with the gauge choice* $\nabla\mathbf{A} = 0$ Among the most common situations let's work out the case of constant fields.

- Constant electric field
$$H = \frac{1}{2}\hat{\mathbf{p}}\hat{\mathbf{p}} - \mathrm{q}\mathbf{E}\mathbf{r}$$
- Constant magnetic field We have
$$\mathbf{A} = \frac{1}{2}\mathbf{r} \times \mathbf{B}$$

and thus

$$\mathbf{A}\hat{\mathbf{p}} = \frac{1}{2}\epsilon_{ijk} r_j B_k \hat{p}_i = -\frac{1}{2}\mathbf{BL} = \hat{\mathbf{p}}\mathbf{A}$$

where the last equality holds since $\hat{\mathbf{p}}$ and $\mathbf{r} \times \mathbf{B}$ commute and $\mathbf{L}$ is the angular momentum operator. Finally

$$H = \frac{1}{2}\hat{\mathbf{p}}\hat{\mathbf{p}} - \frac{\mathrm{q}}{2}\mathbf{BL} + \mathrm{q}^2 \left|\mathbf{r} \times \mathbf{B}\right|^2$$

5.3 Gauge Invariance

See Cohen, complement H_{III} for example. The student must be aware that seemingly different results for the same problem might be related to different gauge choiches and that *any physical observable* must be related to a *gauge invariant* operator.

The lagrangean equation of motion are invariant under gauge transformation

$$\begin{aligned} \Phi &\rightarrow \partial_t \Lambda(\mathbf{r}, t) + \Phi \\ \mathbf{A} &\rightarrow \nabla\Lambda(\mathbf{r}, t) \end{aligned}$$

At the quantized level the Schröedinger equation

$$i\partial_t \psi = \frac{1}{2}(-i\nabla - \mathrm{q}\mathbf{A})(-i\nabla - \mathrm{q}\mathbf{A})\psi + \mathrm{q}\Phi\psi$$

is invariant under gauge transformations provided that we perform the phase transformation

$$\psi \rightarrow \mathrm{e}^{-i\mathrm{q}\Lambda(\mathbf{r},t)}\psi$$

Namely a gauge transformation amount to an (unobservable) phase transformation of the wave function. Notice that only gauge invariant quantities are observable. The canonical momentum $\hat{\mathbf{p}}$ is not a gauge invariant quantity

$$\langle\hat{\mathbf{p}}\rangle\rangle \rightarrow \langle\hat{\mathbf{p}} - i\nabla\Lambda\rangle$$

whereas the mechanical momentum

$$\Pi = \hat{\mathbf{p}} - \mathrm{q}\mathbf{A}$$

is indeed a gauge invariant quantity. It is Π that enters the Ehrenfest theorem

$$m\frac{\mathrm{d}^2 x}{\mathrm{d}t^2} = \dot{\Pi} = \mathrm{q}\left[\mathbf{E} + \frac{1}{2c}\left(\dot{\mathbf{r}} \times \mathbf{B} - \mathbf{B} \times \dot{\mathbf{r}}\right)\right]$$

also the continuity equation is gauge invariant. From the Schröedinger equation we obtain

$$\begin{aligned} \partial_t \rho - \nabla \mathbf{j} &= 0 \\ \mathbf{j} &= \frac{\rho}{m} (\nabla S - \mathrm{q}\mathbf{A}c) \\ \rho &= \sqrt{|\psi|^2} \\ \psi &= \rho \mathrm{e}^{iS} \end{aligned}$$

this is satisfactory since this equation reflects the conservation of the probability.

6 Theory at work

We now provide a few relevant examples to illustrate the applications of the tools discussed in the previous lectures.

6.1 Linear Stark Effect.

Let's now consider the effect of an external constant electric field on a hydrogen atom. We shall consider the linear Stark Effect, namely the effect of a constant electric field on degenerate atomic levels. For definitness we shall discuss the energy level shift of the $n = 2$ level of the hydrogen atom. The potential is

$$V = -eEz$$

which we shall treat as a perturbation of the coulombic potential.

- The $n = 2$ level is fourfold degenerate (we neglect spin) $\Rightarrow$ we need to use perturbation theory for the degenerate case. For this pourpose we evaluate the matrix element of the perturbation *restricted to the invariant* $n = 2$ *subspace*

  $$V_{lm,l'm'} = \langle n = 2, l, m | \, V \, | n = 2, l', m' \rangle$$

  and we diagonalize the resulting matrix

- before proceeding to the actual calculation we try to make best possible use of parity and rotational invariance

- the perturbation is proportional to the coordinate operator, namely it is a *vector operator*. With our choice of the z axis V is the zeroth component of the corresponding rank one spherical operator. The Wigner-Eckart selection rules are

$$\begin{aligned} \Delta m &= 0 \\ \Delta l &= 0, \pm 1 \end{aligned}$$

- *V is odd under parity transformation* and thus only matrix elment connecting odd/even l with even/odd l' are non vanishing $\Rightarrow$

$$\Delta l = \pm 1$$

- Due to the above limitation the only non vanishing matrix elements are

$$\begin{aligned} V_{00;10} &= \langle 2,0,0|\, V\, |2,1,0\rangle = -eE \int \mathrm{d}r\; r^3 R_{20} R_{21} \int \mathrm{d}\Omega \frac{\sqrt{3}}{4\pi} c_\theta^2 \\ &= -eE \int \mathrm{d}r\; \frac{1}{8a_0^4\sqrt{3}} r^3 (2 - \frac{r}{a_0}) \frac{r}{\sqrt{3}} \mathrm{e}^{-r/a_0} \\ &= -\frac{1}{24} eEa_0 \int t^4 (2-t) \mathrm{e}^{-t} = 3eEa_0 \end{aligned}$$

  and its hermitian conjugate

Within the degenerate subspace the perturbative hamiltonian is

$$\tilde{V} = \begin{pmatrix} 0 & V_{00;10} & 0 & 0 \\ V_{10;00} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

where the entries are ordered as $|n=2, l=0, m=0\rangle$, $|2,1,0\rangle$, $|2,1,1\rangle$ and $|2,1,-1\rangle$

The degeneracy is partially lifted:

$$\begin{aligned}
\sqrt{\frac{1}{2}}(|2,1,0\rangle + |2,0,0\rangle) \qquad & \Delta E = 3ea_0E \\
\sqrt{\frac{1}{2}}(|2,1,0\rangle + |2,0,0\rangle) \qquad & \Delta E = -3eEa_0 \\
|2,1,1\rangle \qquad & \Delta E = 0 \\
|2,1,-1\rangle \qquad & \Delta E = 0
\end{aligned}$$

Finally a comment since this has driven some misunderstunding in the past. *The electric field is an external perturbation. Whereas the expression* $\mathbf{Er}$ *is a scalar if the system under consideration is the whole universe, once we restrict the investigation to tha tomic system only* $\mathbf{r}$ *is an operator and* E_j *only a set of numbers. Thus evaluating* $\langle V \rangle$ *V has the structure of a vector operator.*

6.2 Fine structure

6.2.1 Notes for students

Cohen-Tannoudji, chapt. XII. The student is assumed to be able to discuss the simmetries (parity and rotations) of the hamiltonian, to deal with the diagonalization of the spin-orbit term and with the calculation of at least one of the relevant matrix element

6.2.2 Fine structure Hamiltonian

From the non relativistic limit of the Dirac Equation we obtain

$$H = m_e c^2 + \frac{\hat{p}^2}{2m_e} + V(R) - \frac{\hat{p}^4}{8m_e^3c^2} + \frac{1}{2m_e^2c^2}\frac{1}{R}\frac{\mathrm{d}V}{\mathrm{d}R}\mathbf{L}\cdot S + \frac{\hbar^2}{8m_e^2c^2}\Delta V(R)$$

Let's recall a few useful quantities

- $E_I = \frac{1}{2}\alpha^2 mc^2$. Ground state energy
- $a_0 = \frac{1}{\alpha}\lambda\!\!\!^{-}_c$ Bohr radius
- $\alpha = \frac{e^2}{\hbar\, c} \sim \frac{1}{137.}$ fine structure constant.

- $\lambda = \frac{\bar{h}}{mc}$ is the compton wave length.

Let's comment briefly on the origin of the various terms.

- $m_e c^2$. Electron rest energy. It is a constant term and it just shifts all energy levels by a constant. No observable effect
- $\frac{\hat{p}^2}{2m_e} + V(R)$. The non relativistic hamiltonian.
- $W_{mv} = \frac{\hat{p}^4}{8m_e^3 c^2}$. The first relativistic correction to kinetic energy. The relative order of magnitude is

$$\frac{W_{mv}}{H_0} \sim \frac{\hat{p}^2}{4m_e^2 c^2} \sim \frac{\hat{\hbar}^2}{4a_0^2 m_e^2 c^2} \sim \alpha^2$$

- $W_{SO} = \frac{1}{2m_e^2 c^2} \frac{1}{R} \frac{\mathrm{d}V}{\mathrm{d}R} \mathbf{L} \cdot S$ Spin orbit interaction. Classically we picture the atom as an electron orbiting around the proton. A charge moving into a static electric field feels a magnetic field

$$\mathbf{B} = -\frac{1}{c^2} \mathbf{v} \times \mathbf{E}$$

Because of the electron intrinsic magnetic moment

$$\mathbf{M} = \frac{q\mathbf{S}}{m_e}$$

this implies an interaction term

$$H_I = -\mathbf{M}\mathbf{B}$$

The electrostatic field is

$$\mathbf{E} = \nabla V(R) = -\nabla \frac{e^2}{r} = -\frac{1}{q} \frac{\mathrm{d}V}{\mathrm{d}r} \frac{\mathbf{r}}{r}$$

and thus

$$\mathbf{B} = \frac{1}{qc^2} \frac{1}{r} \frac{\mathrm{d}V}{\mathrm{d}r} \frac{\hat{\mathbf{p}}}{m_e} \times r = \frac{1}{qm_e c^2} \frac{1}{r} \frac{\mathrm{d}V}{\mathrm{d}r} \mathbf{L}$$

and finally

$$H_I = \frac{e^2}{m_e^2 c^2} \frac{1}{R^3} \mathbf{L} \cdot \mathbf{S}$$

which is up to a factor 1/2 the spin orbit term. The factor 1/2 can be understood classically observing that the spin precesses around the effective magnetic field. The relativistic Dirac equation do provide the correct term. The realtive order of magnitude is given

$$\frac{W_{SO}}{H_0} \sim \hbar^2 m_e^2 c^2 a_0^2 \sim \alpha^2$$

$(\mathbf{L} \sim \mathbf{S} \sim \hbar)$

- $W_D = \frac{\hbar^2}{8m_e^2c^2}\Delta V(R)$, the Darwin term. This is a genuine relativistic effect. In the equation it appears a non local term. The electron feels the effect of the value of the field in a domain located around the electron position $\mathbf{r}$ and of size λ. $(\tilde{V}(\mathbf{r}) = \int f(\mathbf{x})V(\mathbf{x}+\mathbf{r}) \sim V(\mathbf{r}) + \Delta V(\mathbf{r})|\mathbf{x}-\mathbf{r}|^2)$ With $V(r) = 1/r$ for the Darwin term we obtain

$$W_D = \frac{\hbar^2}{8m_e^2c^2}\Delta\frac{1}{R} = \frac{\hbar^2}{8m_e^2c^2}\delta(\mathbf{r})$$

Taking the mean value of the darwin term on an atomic state we find a contribution

$$\frac{\pi e^2 \hbar^2}{2m_e c^2}\left|\psi(0)\right|^2$$

which is non zero only for s states. Since $\psi(0) \sim a_0^{-3/2}$ the relative order of magnitude of the Darwin term is

$$\frac{W_D}{H_0} \sim \alpha^2$$

6.3 Fine structure splitting, n=2 level

Taking into account electron and proton spin there are 16 states. The fine strucutre hamiltonian doesn't invole proton spin: we shall have a twofold degenarcy. The remaining eight level are splitted by fine structure terms.

Let's start from the *velocity term*. $W_{mv} \sim \hat{p}^4$. W_{mv} commute with L^2 and L_z, and it does't depend on spin. It will therefore be diagonal in L^2, L_z, S^2, S_z space and the shift will be degenerate for p states and for s states. We have

$$\hat{p}^4 = 4m_e^2[H_0 - V]^2$$

and thus

$$\langle n,l,m|\, p^4\, |n,l,m\rangle = 4m_e^2\langle [H_0 - V]^2\rangle - \frac{1}{2m_e c^2}\left[E_n^2 + 2E_n e^2\langle 1/R\rangle + e^4\langle 1/R^2\rangle\right]$$

the angular integral is one and the radial part is readily evaluated to

$$\begin{aligned}\langle\rangle_{1s} &= \frac{1}{2a_0^2}\\ \langle\rangle_{2s} &= \frac{1}{4a_0^2}\\ \langle\rangle_{2p} &= \frac{1}{12a_0^2}\end{aligned}$$

and thus

$$\begin{aligned}\langle W_{mv}\rangle_{1s} &= -\frac{5}{8}\alpha^4 m_e c^2\\ \langle W_{mv}\rangle_{2s} &= -\frac{13}{128}\alpha^4 m_e c^2\\ \langle W_{mv}\rangle_{2p} &= \frac{7}{384}\alpha^4 m_e c^2\end{aligned}$$

The perturbation is already diagonal and lifts the degeneracy among $2s$ and $2p$.

The Darvin Term is non zero only for s states

$$\begin{aligned}\langle W_D\rangle_{1s} &= \frac{1}{2}\alpha^4 m_e c^2\\ \langle W_D\rangle_{2s} &= -\frac{1}{16}\alpha^4 m_e c^2\end{aligned}$$

The spin orbit term depends on spin and angular momentum. $W_{SO} = \frac{1}{2m_e^2c^2}\frac{1}{R}\frac{\mathrm{d}V}{\mathrm{d}R}\mathbf{L}\cdot\mathbf{S}$ The spin orbit term commute with L^2, S^2 but not with L_z and S_z. Thus there is no mixing among s and p states but there is mixing among states with different L_z and S_z. In principle we should evaluate the matrix element of the spin-orbit term and then diagonalize it. We are however familiar with similar operators. The hamiltonian of the atom is invariant under simultaneous rotation *of all tensorial quantities* $\mathbf{r}$, $\mathbf{S}$, ... thus it is

diagonal in the $|j, l, s, j_z\rangle$ basis. The $2p$ states split into $2p_{1/2}$ and $2p_{3/2}$ respectively with two and four degenerate state. The states $2s$ is unaffected since $\mathbf{L} = 0$ for this states. The contribution of W_{SO} term is readily evaluated in this basis

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

which leads to an energy split

$$\begin{aligned} \delta E_{1/2} &= \frac{-1}{48} m_e c^2 \alpha^4 \\ \delta E_{3/2} &= \frac{1}{96} m_e c^2 \alpha^4 \end{aligned}$$

Notice that the average over all states of the shift is zero. Since there is clearly no preferred direction in space the average $\langle J_z \rangle$ must be zero.

Collecting all the contributions it turns out that the levels $2s_{1/2}$ and $2p_{1/2}$ are degenerate whereas the $2p_{3/2}$ is higher. Within our present discussion this is an accidental coincidence. The relativistic Dirac Equation has however additional symmetries and it turns out that the energy levels do depend only on J and thus this degeneration is exact to all orders.

Notice that both the velocity term and the Darwin term don't depend on spin and they are scalars. Both contributions depends only on l. Thus our calculation is unaffected when we move to the $|j, l, s, j_z\rangle$ base.

6.4 Hyperfyne splitting

we shall now include the proton spin into our considerations

6.4.1 The hyperfine Hamiltonian

The proton is itself a spin 1/2 particle and thus it has an intrinsic magnetic moment

$$\boldsymbol{\mu}_p = \frac{g_p \mu_n \mathbf{S}_p}{\hbar} = \frac{q_p \hbar}{2M_p} \frac{g_p \mathbf{S}_p}{\hbar}$$

where μ_n is the nuclear Bohr magneton and $g_p (\sim 5.585)$ is the proton giromagnetic ratio.

The elecron thus moves also in the magnetic field originated by the proton magnetic dipole moment. The corresponding *magnetic hyperfine hamiltonian* is

$$W_{hf} = -\frac{\mu_0}{4\pi}\left\{\frac{q}{m_e R^3}\mathbf{L}\boldsymbol{\mu}_p + \frac{1}{R^3}\left[3(\boldsymbol{\mu}_e\cdot\mathbf{n})(\boldsymbol{\mu}_p\cdot\mathbf{n}) - \boldsymbol{\mu}_p\boldsymbol{\mu}_e\right] + \frac{8\pi}{3}\boldsymbol{\mu}_p\boldsymbol{\mu}_e\delta(\mathbf{r})\right\}$$

where the first term is the interaction of the nuclear magnetic dipole moment, the second term originates from the dipole-dipole interaction between electonic and nuclear magnetic moment and the last term originates from the singularity at $\mathbf{r} = 0$ from the vector potential of the proton. The relative order of magnitude of the hyperfine hamiltonian is

$$\frac{W_{hf}}{W_{SO}} \sim \frac{m_e}{m_p}$$

much smaller than the fine strucutre terms.

6.4.2 Hyperfine splitting of $1s$ state

The fine structure hamiltonian just results in an overall shift of the level

$$\delta E = \frac{1}{8}m_e c^2\alpha^4$$

since $\langle W_{SO}\rangle = 0$ for $1s$ states ($l = 0$) and the other terms don't depend on electron or proton spin.

Let's evaluate the effect of the hyperfine hamiltonian which we shall treat as a perturbation. The ground state is fourfold degenerate (two spin degrees of freedom for both the electron and the proton) we thus need to use perturbation theory in the degenerate case. We thus need to evaluate

$$\langle l = 0, S_{ze}, S_{zp}|\, W_{hf}\, \big|l = 0, S'_{ze}, S'_{zp}\rangle$$

and diagonalize the corresponding matrix.

The first term of the hyperfine hamiltonian is zero since $l = 0$ For the dipole-dipole term we have

$$W_{hf;d} = 3(\boldsymbol{\mu}_e\cdot\mathbf{n})(\boldsymbol{\mu}_p\cdot\mathbf{n}) - \boldsymbol{\mu}_p\boldsymbol{\mu}_e = 3\mu_{ej}\mu_{pk}\left(n_j n_k - \frac{1}{3}\delta_{jk}\right)$$

the contribution to the matrix element is

$$\langle l=0, S_{ze}, S_{zp}| W_{hf;d} \left|l=0, S'_{ze}, S'_{zp}\right\rangle = 3 \langle l=0| \left(n_j n_k - \frac{1}{3}\delta_{jk}\right) |l=0\rangle \langle S_{ze}, S_{zp}| \mu_{ej}\mu_{pk} \left|S'_{ze}, S'_{zp}\right\rangle$$

Now

$$\langle l=0| \left(n_j n_k - \frac{1}{3}\delta_{jk}\right) |l=0\rangle$$

is the matrix element of a rank two tensor among two heigenstates of l and l_z. It's average value over an $l=0$ state is zero due to the Wigner-Eckart theorem. It can also be explicitly verified that

$$\int \mathrm{d}\Omega\ n_x^2 = \int \mathrm{d}\Omega\ n_y^2 = \int \mathrm{d}\Omega\ n_z^2 = \frac{1}{3}\int \mathrm{d}\Omega 1$$

whereas off-diagonal terms are zero because of $\mathrm{d}\phi$ integration. We are left only with the contact term

$$-\frac{2\mu_0}{3} \langle n=1, l=0, l_z=0, m_s, m_I| \boldsymbol{\mu}_p \cdot \boldsymbol{\mu}_e |n=1, l=0, l_z=0, m'_s, m'_I\rangle$$
$$= \frac{4}{3\hbar^2} g_p \frac{m_e}{M_p} m_e c^2 \alpha^4 \langle m_s, m_I| \mathbf{SI} |m'_s, m'_I\rangle = \mathcal{A} \langle m_s, m_I| \mathbf{SI} |m'_s, m'_I\rangle$$

We already know how to diagonalize this term. We shall have a triplet ($F = I+S = 1$) state and a singlet ($F=0$) state with energy split $\Delta E_{F=1} = 1/4\mathcal{A}\hbar^2$ $\Delta E_{F=0} = -3/4\mathcal{A}\hbar^2$ respectively.

7 Fine structure splitting and Zeman effect for the 2n level

We have already discussed the impact of spin orbit terms. Let's now consider the effect of an external constant magnetic field. The Zeeman Hamiltonian is (neglecting nuclear magnetic moment)

$$H_z = \mu_B B_0 (L_z + 2S_z) = -\mu_B B_0 (J_z + S_z)$$

The overall hamiltonian is now invariant only for rotation around the z axis and the degeneracy will be (partially) removed. H_z is Parity invariant and thus s and p states don't mix. The s states are lifted by an energy shift

$\Delta E_{1s} = \pm\mu_B B_0$. p states do mix among themselves. J_z is still a good quantum number and thus the only non vanishing matrix element are

$$\begin{aligned}
\langle 3/2, \pm 3/2 | H_Z | 3/2, \pm 3/2 \rangle &= \mp 2\mu_B B_0 \\
\langle 3/2, \pm 1/2 | H_Z | 3/2, \pm 1/2 \rangle &= \mp \frac{2}{3}\mu_B B_0 \\
\langle 1/2, \pm 1/2 | H_Z | 1/2, \pm 1/2 \rangle &= \mp \frac{1}{3}\mu_B B_0 \\
\langle 3/2, \pm 1/2 | H_Z | 1/2, \pm 1/2 \rangle &= \mp \frac{\sqrt{2}}{3}\mu_B B_0
\end{aligned}$$

where we have used

$$\begin{aligned}
|3/2, 1/2\rangle &= \sqrt{\frac{2}{3}} |l_z = 0, s_z = 1/2\rangle + \sqrt{\frac{1}{3}} |l_z = 1, s_z = -1/2\rangle \\
|1/2, 1/2\rangle &= -\sqrt{\frac{1}{3}} |l_z = 0, s_z = 1/2\rangle + \sqrt{\frac{2}{3}} |l_z = 1, s_z = -1/2\rangle \qquad (6)
\end{aligned}$$

and the problem can be solved exactly. Including the fine splitting contributions the perturbing hamiltonian is

$$W = H_{Magnetic} + H_{finestructure}$$

which has the only non vanishing entries

$$\begin{aligned}
\langle j = 3/2, l = 1, j_z = \pm 3/2 | H_Z | j = 3/2, l = 1, j_z = \pm 3/2 \rangle &= \delta_{FS} \mp 2\mu_B B_0 \\
\langle j = 3/2, l = 1, j_z = \pm 1/2 | H_Z | j = 3/2, l = 1, j_z = \pm 1/2 \rangle &= \delta_{FS} \mp \frac{2}{3}\mu_B B_0 \\
\langle j = 1/2, l = 1, j_z = \pm 1/2 | H_Z | j = 1/2, l = 1, j_z = \pm 1/2 \rangle &= -\delta_{FS} \mp \frac{1}{3}\mu_B B_0 \\
\langle j = 3/2, l = 1, j_z = \pm 1/2 | H_Z | j = 1/2, l = 1, j_z = \pm 1/2 \rangle &= \mp \frac{\sqrt{2}}{3}\mu_B B_0 \\
\langle j = 1/2, l = 0, j_z = \pm 1/2 | H_Z | j = 1/2, l = 0, j_z = \pm 1/2 \rangle &= -\delta_{FS} \qquad (7) \\
& \qquad (8)
\end{aligned}$$

where δ_{FS} is the fine splitting term.

One can also approach perturbatively the two limits: weak field (Zeeman splitting) and strong field (Paschen-Back).

Weak field, Zeeman effect

$$\mu_B B_0 \ll \delta_{FS}$$

the magnetic hamiltonian is a perturbation with respect to the fine splitting one. Thus we choose as basis $|j, l, s, j_z\rangle$ and to first order in $\mu_B B_0/\delta_{FS}$ the energy level splitting is given by the diagonal entries in eqn. /refeq:zeeman-fs. Notice that off-diagonal terms connects *different* energy levels ($j = 3/2$ and $j = 1/2$) and therefore don't contribute to first order.

Strong field, Paschen-Back effect

$$\mu_B B_0 \gg \delta_{FS}$$

Now it is the fine splitting hamiltonian which is a perturbation with respect to the magnetic one. We choose a basis that *diagonalize* the magnetic hamiltonian, $|l, s, l_z, s_z\rangle$. The Zeeman hamiltonian splits the n=2 level into five energy levels

$$\delta E = \pm 2\mu_0 B \quad |l = 1, l_z = \mp 1, s_z = -\mp 1/2\rangle$$

$$\delta E = \pm \mu_0 B \begin{cases} |l = 1, l_z = 0, s_z = \mp 1/2\rangle \\ |l = 0, l_z = 0, s_z = \mp 1/2\rangle \end{cases}$$

$$\delta E = 0 \begin{cases} |l = 1, l_z = 1, s_z = -1/2\rangle \\ |l = 1, l_z = -1, s_z = 1/2\rangle \end{cases}$$

Within the three degenerate subspaces the fine splitting hamiltonian is diagonal since off diagonal elements are prevented either from parity or j_z non conservation. For the diagonal terms, using the inverse of eqn. 6, We obtain

$$\begin{aligned}
\langle l = 1, l_z = \pm 1, s_z = \pm 1/2| \, H_{FS} \, |l = 1, l_z = \pm 1, s_z = \pm 1/2\rangle &= \delta_{FS} \\
\langle l = 1, l_z = \pm 1, s_z = \mp 1/2| \, H_{FS} \, |l = 1, l_z = \pm 1, s_z = \pm 1/2\rangle &= -\frac{1}{3}\delta_{FS} \\
\langle l = 1, l_z = 0, s_z = \pm 1/2| \, H_{FS} \, |l = 1, l_z = 1, s_z = \pm 1/2\rangle &= +\frac{1}{3}\delta_{FS} \\
\langle l = 0, l_z = 0, s_z = \pm 1/2| \, H_{FS} \, |l = 0, l_z =, s_z = \pm 1/2\rangle &= -\delta_{FS}
\end{aligned}$$

which are the required energy level shifts to first order in $\delta_{FS}/\mu_0 B$

8 Hyperfine splitting of the $2n$ level

We shall first consider the hyperfine hamiltonian as a perturbation. Let's consider the first term. It commutes with L^2 and thus it connects only states with the same l. It vanishes for $s_{1/2}$ states. It doesn't depend on electron spin which can thus be neglected. It doesn't commute with J_z and thus we can expect it mixes all the p terms.

9 Time dependent perturbation theory

9.1 Note for students

Sakurai chap. 5.5. Cohen ?? Sakurai approaches the solution of the problem using the Dyson series. Whereas Dyson series plays an important role in the contest of relativistic system is overly redundant for low energy QM. Follow the simplest approach outlined here.

9.2 Time dependent perturbation theory

Let's consider the Schröedinger equation

$$i\partial_t \left|\psi\right\rangle = \left[H_0 + V(t)\right]\left|\psi\right\rangle$$

where H_0 doesn't depend on t and we assume that it's eigenvalues and eigenvectors are known.

$$H_0 \left|\psi_n\right\rangle = E_n \left|\psi_n\right\rangle$$

we move to the so called interaction picture.

$$\begin{aligned}
\left|\psi\right\rangle_I &= \mathrm{e}^{iH_0 t}\left|\psi\right\rangle \\
\left|\psi_n\right\rangle &= \mathrm{e}^{-iE_n t}\left|\psi_n\right\rangle_I \\
i\partial_t\left|\psi\right\rangle_I &= V_I\left|\psi\right\rangle_I \\
V_I &= \mathrm{e}^{iH_0 t}V(t)\mathrm{e}^{-iH_0 t} \\
V_{Ilm} &= \mathrm{e}^{i(E_l - E_m)t}V_{lm}
\end{aligned}$$

Let's follow the evolution of a state in the interaction picture

$$\begin{aligned}
i\partial_t\left|\psi\right\rangle_I &= V(t)\left|\psi\right\rangle \Rightarrow \left\langle\psi_m\right|\left[i\partial_t - V_I(t)\right]c_n(t)\left|\psi_n\right\rangle = 0 \\
&\Rightarrow i\dot{c}_m = \left\langle\psi_m\right|\mathrm{e}^{-iH_0 t}V(t)\mathrm{e}^{iH_0 t}\left|\psi_n\right\rangle \Rightarrow \dot{c}_m(t) = -i\mathrm{e}^{i(E_m - E_n)t}c_n(t) \quad (9)
\end{aligned}$$

Insofar everything is exact, at zeroth order in perturbation theory we have

$$\dot{c}_n^{(0)} = 0 \Rightarrow c_n^{(0)} = c_n(t = t_0)$$

at first order in perturbation theory we shall have

$$c_m^{(1)} = -ic_n^{(0)} \int_{t_0}^{t} V_{mn}(s) \mathrm{e}^{i(E_m - E_n)s} \mathrm{d}s \tag{10}$$

Notice that the results in eqns. 9 and 10 are in the interaction representation:

$$|\psi\rangle_I = c_n(t) \, |\psi\rangle_n$$

to move back to the Schröedinger equation we have

$$|\psi\rangle_S = \mathrm{e}^{-iH_0 t} |\psi\rangle_I = c_n(t) \mathrm{e}^{-iE_n t} \, |\psi\rangle_n$$

If the initial state is not an eigenstate of the H_0 its crucial to retain these additional phase factors.

9.3 Two level problem with an oscillating potential, Rabi's formula

We want to solve the problem

$$i \begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \end{pmatrix} = \begin{pmatrix} \frac{\Delta}{2} & \gamma \mathrm{e}^{i\omega t} \\ \gamma \mathrm{e}^{-i\omega t} & -\frac{\Delta}{2} \end{pmatrix}$$

Using $a_{1,2} = c_{1,2} \mathrm{e}^{\pm i\omega t/2}$ the equation becomes

$$i \begin{pmatrix} \dot{a}_1 \\ \dot{a}_2 \end{pmatrix} = \begin{pmatrix} \frac{\Delta - \omega}{2} & \gamma \\ \gamma & -\frac{\Delta - \omega}{2} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

which can be solved exactly. If in the initial state the system is in the state

$$|\psi(t = 0)\rangle = |1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

at the time t the probability $\mathcal{P}_2$ to find the system in the state $|2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ is

$$\begin{aligned} \mathcal{P}_2 &= |c_2(t)|^2 = \frac{\gamma^2}{\gamma^2 + (\Delta - \omega)^2/4} \sin^2 \left\{ \left[\gamma^2 + \frac{(\Delta - \omega)^2}{4} \right] \right\} \\ \mathcal{P}_1 &= |c_1(t)|^2 = 1 - |c_2(t)|^2 \end{aligned}$$

- Notice that the above formula (Rabi's formula) is valid only with the given initial condition. Try with $|\psi(t=0)\rangle = (a\ b)$.
- If $\Delta = \omega$ we have the resonant condition. The amplitude of the oscillation is maximal (and equal to one)
- If the resonant condition is fulfilled the system jumps continuosly between the state $|1\rangle$ and $|2\rangle$. This is a cycle of stimulated absorption/emission. The potential acts as a source/well of energy