PERTURBATION THEORY (TIME-INDEPENDENT)

Both the Zeeman effect and the spin-orbit interaction are a special case of the following general problem:

Let us suppose that we solved the Schroedinger's equation (time-independent equation) for some system with Hamiltonian H^0.

That is, we found the eigenstates ψ_n^0 and their corresponding eigenvalue E_n^0, such that:

$$\underset{\text{operator}}{H^0}\,\psi_n^0 = \underset{\text{number}}{E_n^0}\,\psi_n^0$$

The ψ_n^0 form a complete set of orthonormal eigenstates:

orthonormality:

$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm} \quad \left(\text{Kronecker delta: } \delta_{nm} = \begin{cases} 1 & \text{if } n=m \\ 0 & \text{if } n \neq m \end{cases}\right)$$

completeness:

$$\underset{\text{generic state}}{\psi} = \sum_n a_n \psi_n^0$$

<u>any</u> generic state of the system can be written as a linear combination (with possibly <u>complex</u> coefficients) of the eigenstates ψ_n^0

Let us now add a small perturbation to the Hamiltonian H^0, which we call λH^1 (the idea being that λ is a small number).

Our new Hamiltonian is:

$$H = H^0 + \lambda H^1$$

Question: what can we say about the eigenstates and eigenvalues of H, i.e., the ψ_n and E_n that satisfy:

$$H \psi_n = E_n \psi_n$$

Example: Zeeman effect on Hydrogen atom:

$$H^0 = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\varepsilon r} \qquad E_n^0 = -\frac{13.6}{n^2}\ \text{eV}$$

$$\lambda H^1 = -\vec{\mu}\cdot\vec{B}$$

special case because the eigenstates of H^0 (quantum numbers: n, ℓ, m) also happen to be eigenstates of $\lambda H'$. We did not need to do anything special, just calculate the contribution of the $-\vec{\mu}\cdot\vec{B}$ piece to the energy E_n^0 (note: we did take $\vec{B} = B_z\hat{z}$ so that m was a good quantum number).

Let us do the more general case by finding a way to write the effect of the perturbation on the Hamiltonian eigenstates and eigenvalues as an expansion series. The basic idea is that if $\lambda H'$ is small compared to H^0, then also ψ_n^0 and E_n^0 will change only a little.

Let us then write ψ_n and E_n as a power series in λ:

$$\psi_n = \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + \lambda^3\psi_n^3 + \ldots$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \lambda^3 E_n^3 + \ldots$$

this ^{3} is an exponent: $\lambda\cdot\lambda\cdot\lambda$

the ^{3} here is just an index: this is the third-order correction to E_n.

Let us not overthink about what λ's value is; it helps us identify the order of each contribution, but we can crank it up to 1 without losing generality. Let us just keep in mind that our Hamiltonian, if $\lambda \to 1$, becomes $H = H^0 + H^1$, and H' is small.

Let us use the expression for ψ_n and E_n as a λ power series:

$$H \psi_n = E_n \psi_n$$

$$(H^0 + \lambda H') \quad (\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots) \qquad (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots)$$

Let us now collect the pieces with the same power of λ:

λ^0: $\quad H^0 \psi_n^0 = E_n^0 \psi_n^0$ $\quad$ this is satisfied: it is the Schroedinger's equation of the unperturbed Hamiltonian!

λ^1: $\quad H^0 \psi_n^1 + H^1 \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$

λ^2: $\quad H^0 \psi_n^2 + H^1 \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0$

$\vdots$

Let us take the λ^1 order equation and take its inner product with ψ_n^0.
That is, let us multiply by ψ_n^{0*} and integrate. In Dirac's notation:

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle = \underbrace{\langle \psi_n^0 | E_n^0 \psi_n^1 \rangle}_{E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle} + \underbrace{\langle \psi_n^0 | E_n^1 \psi_n^0 \rangle}_{E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle}$$

H^0 Hermitian:

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle = \langle H^0 \psi_n^0 | \psi_n^1 \rangle$$
$$= E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle$$

The first terms on the left and right sides are identical, and cancel out.
In the right side I also have $\langle \psi_n^0 | \psi_n^0 \rangle = 1$ (normalization).
Here comes the fundamental result of perturbation theory:

$$\boxed{E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle}$$ (note I put $\lambda = 1$, not needed anymore)

The first-order correction to the energy eigenvalue is the expectation value of the perturbation H' calculated on the unperturbed state