Quantum Mechanics 2

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4 Chapter 7: Time-independent perturbation theory

Learning Goals

- To determine in a systematic manner the **higher-order corrections** to the energies and state vectors of an unperturbed quantum system by means of perturbation theory.
- To assess the criteria that determine the conditions whereby a certain perturbative expansion can be expected to be **convergent**.
- To identify the conditions of applicability of the perturbative techniques in the case of **degenerate spectra.**
- To compute the first non-trivial corrections to the **energy levels of the hydrogen atom**, arising from relativistic effects and from the spin-orbit interactions.

In this section of the lecture notes we present the main concepts discussed in **Chapter 7 ("Time-Independent Perturbation Theory")** of the course textbook. The goal of these lecture notes is to provide a self-consistent study resource for the students, which is then complemented by the live lectures (and their recordings), the tutorial sessions, as well as their own study of the textbook. The relevant textbook sections are indicated below, material from other sections not listed there will not be required for the examination.

Textbook sections

- **7.1**: Non-degenerate Perturbation Theory.
- **7.2**: Degenerate Perturbation Theory.
- **5.3**: The Fine Structure of Hydrogen.

The number of quantum mechanical systems that can be solved in an **analytic closed form** is unfortunately rather small. With a few exceptions, in general we will need to carry out some approximation in order to solve a given problem in quantum mechanics. The virtue of **perturbation theory** is that, starting from the known solutions to a simpler ("unperturbed) problem, it makes possible determining systematically and in a fully controllable manner the corrections that modify the unperturbed results. In other words, perturbation theory is a systematic procedure for obtaining approximate solutions to the perturbed problem, by building on the exact known solutions to the unperturbed case. The higher the number of terms we include on this series expansion, the better our estimate of the full energies and wave functions will be. Perturbation theory is extremely valuable in quantum mechanics, and here we will illustrate its use with different examples including the calculation of the **fine structure of hydrogen**.

4.1 Non-degenerate perturbation theory

Let us assume that we have some quantum system that we have been able to solve **exactly**. Some instances of exactly-solvable systems that you have encountered so far are the infinite square and spherical well potentials, the quantum harmonic oscillator in 1D and 3D, and the hydrogen atom. By solving the system we mean finding the eigenvalues and eigenvectors of the corresponding Schroedinger equation, which in full generality can be expressed as

$$\hat{H}^{(0)}\big|\psi_k^{(0)}\big\rangle = E_k^{(0)}\big|\psi_k^{(0)}\big\rangle\,, \tag{4.1}$$

where the superindices $^{(0)}$ indicate that these are the **exact solutions to the unperturbed Hamiltonian** $\hat{H}^{(0)}$. As usual, the eigenvectors of this unperturbed Hamiltonian will be orthonormal,

$$\langle\psi_k^{(0)}|\psi_l^{(0)}\rangle = \delta_{kl}\,. \tag{4.2}$$

The exact solutions of the unperturbed Hamiltonian Eq. (4.1) are a necessary starting point of the perturbative method: if these are not available, the perturbative expansion is not applicable.

Degenerate vs non-degenerate problems

Although it might not seem a big deal at this point, the derivation that follows is only guaranteed to work if the unperturbed Hamiltonian $\hat{H}^{(0)}$ has associated a **non-degenerate spectra** where if $j \neq k$ then $E_k^{(0)} \neq E_j^{(0)}$. The presence of degeneracies in the energy spectrum introduces problems that we will discuss how to tackle later in this chapter.

Now consider that we modify the original potential in the unperturbed Hamiltonian Eq. (4.1) in the following manner

$$V(x) = V^{(0)}(x) + \delta V(x)\,, \tag{4.3}$$

where $\delta V(x)$ is some **small correction** with respect to the original potential energy $V^{(0)}(x)$. We will quantify soon what exactly do we mean by this "smallness" requirement. We want to solve the new Schroedinger equation in terms of the new eigenvalues and eigenvectors

$$\hat{H}\big|\psi_k\big\rangle = E_k\big|\psi_k\big\rangle \quad \text{where} \quad \hat{H} = \hat{H}^{(0)} + \delta V(x) \tag{4.4}$$

where we have removed the superindices to indicate that now eigenvalues and eigenvectors refer to the full Hamiltonian. We will do this by using **perturbation theory** under the assumption that $\delta V(x)$ will only modify in a moderate manner the original eigenvalues and eigenvectors (of course, if you know how to solve exactly Eq. (4.4), perturbation theory is irrelevant!).

With this motivation, let us express the new, perturbed Hamiltonian as

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}' \,, \tag{4.5}$$

where λ is a **small dimensionless parameter**. Note that the kinetic term is not modified by the change in the potential energy, and hence we will have that $\lambda \hat{H}' = \delta V(x)$. Since λ is a small dimensionless parameter, it seems sensible to express both the new wave function and the corresponding energies in terms of a **series expansion** in λ, starting from the original (unperturbed) values:

$$\begin{aligned} \big|\psi_n\big\rangle &= \big|\psi_n^{(0)}\big\rangle + \lambda\big|\psi_n^{(1)}\big\rangle + \lambda^2\big|\psi_n^{(2)}\big\rangle + \mathcal{O}\left(\lambda^3\right) \,, \\ E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \mathcal{O}\left(\lambda^3\right) \,. \end{aligned} \tag{4.6}$$

Some comments about this expansion are relevant now:

- $\big|\psi_n^{(1)}\big\rangle$ and $E^{(1)}$ are known as the **first-order corrections** to the state vector and the energies, $\big|\psi_n^{(2)}\big\rangle$ and $E^{(2)}$ are known as the **second-order corrections** and so on.
- Each subsequent term in this series is **suppressed** by a factor of the small expansion parameter λ as compared to the previous one.[14]
- The more terms in the expansion in λ we include, in principle the better estimate to the full result that we can expect. The number of required terms to obtain a reliable approximation depends, among other things, on the value of λ.
- If λ is small enough, this series expansion is guaranteed to represent a good approximation: in the $\lambda \to 0$ limit then $\hat{H} \to \hat{H}^{(0)}$ and the wave function and energies reduced to the original (unperturbed) values.

We can now try to insert these perturbative expansions, Eq. (4.6) into the original Schroedinger equation, we thus obtain:

$$\left(\hat{H}^{(0)} + \lambda \hat{H}'\right)\left(\big|\psi_n^{(0)}\big\rangle + \lambda\big|\psi_n^{(1)}\big\rangle + \lambda^2\big|\psi_n^{(2)}\big\rangle + \ldots\right) \tag{4.7}$$

$$= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots\right)\left(\big|\psi_n^{(0)}\big\rangle + \lambda\big|\psi_n^{(1)}\big\rangle + \lambda^2\big|\psi_n^{(2)}\big\rangle + \ldots\right) \tag{4.8}$$

The key idea underlying perturbation theory is to collect terms at the **same order** in the expansion in the small parameter λ, and solve the corresponding equations in a sequential manner: first we solve the corrections to the energies and the state vectors at $\mathcal{O}(\lambda)$, then at $\mathcal{O}\left(\lambda^2\right)$ and so on. Recall that $\mathcal{O}\left(\lambda^0\right)$ corresponds to the unperturbed result which we assume has already been solved/

By collecting the terms proportional to λ^0, λ^1, and λ^2 we find the following relations:

$$\hat{H}^{(0)}\big|\psi_k^{(0)}\big\rangle = E_k^{(0)}\big|\psi_k^{(0)}\big\rangle \qquad \left[\text{order } \lambda^0\right] \tag{4.9}$$

$$H^{(0)}\big|\psi_k^{(1)}\big\rangle + H'\big|\psi_k^{(0)}\big\rangle = E_k^{(0)}\big|\psi_k^{(1)}\big\rangle + E_k^{(1)}\big|\psi_k^{(0)}\big\rangle \qquad \left[\text{order } \lambda^1\right] \tag{4.10}$$

$$H^{(0)}\big|\psi_k^{(2)}\big\rangle + H'\big|\psi_k^{(1)}\big\rangle = E_k^{(0)}\big|\psi_k^{(2)}\big\rangle + E_k^{(1)}\big|\psi_k^{(1)}\big\rangle + E_k^{(2)}\big|\psi_k^{(0)}\big\rangle \qquad \left[\text{order } \lambda^2\right] \tag{4.11}$$

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[14] Actually in many cases the perturbative series are only **asymptotic**, meaning that at some point including higher-order terms in the expansion degrades, rather than improves, the agreement with the exact result.

The first of these relations, Eq. (4.9) was our starting point (the Schroedinger equation for the unperturbed system, we we assume to be solvable and known). Solving Eq. (4.10) will allow us to evaluate the first-order corrections to the unperturbed state vectors and the energies.

Notice also the neat property of the perturbative relations: the equation for $E_k^{(1)}$ and $\left|\psi_k^{(1)}\right\rangle$ relies only on the knowledge of $E_k^{(0)}$ and $\left|\psi_k^{(0)}\right\rangle$, while the relation for $E_k^{(2)}$ and $\left|\psi_k^{(2)}\right\rangle$ relies on the knowledge of both $E_k^{(0)}$ and $\left|\psi_k^{(0)}\right\rangle$ as well as $E_k^{(1)}$ and $\left|\psi_k^{(1)}\right\rangle$. This structure indicates that the perturbation theory technique must the applied in a **sequential manner**: unless I compute the first-order corrections, there is no way I may attempt to evaluate the second-order corrections.

4.1.1 First-order perturbation theory

Given that the leading order (unperturbed) problem is solved, let us now attempt to solve Eq. (4.10) and determine the $\mathcal{O}(\lambda)$ corrections to the energy $E_k^{(1)}$ and the state vector $|\psi_k^{(1)}\rangle$, and use them to improve the unperturbed $\mathcal{O}(\lambda^0)$ results. The starting point is Eq. (4.10):

$$H^{(0)}\left|\psi_k^{(1)}\right\rangle + H'\left|\psi_k^{(0)}\right\rangle = E_k^{(0)}\left|\psi_k^{(1)}\right\rangle + E_k^{(1)}\left|\psi_k^{(0)}\right\rangle \tag{4.12}$$

We can now multiply from the left by the bra $\left\langle\psi_k^{(0)}\right|$ to obtain the following scalar equation

$$\left\langle\psi_k^{(0)}\middle|\hat{H}^{(0)}\psi_k^{(1)}\right\rangle + \left\langle\psi_k^{(0)}\middle|\hat{H}'\psi_k^{(0)}\right\rangle = E_k^{(0)}\left\langle\psi_k^{(0)}\middle|\psi_k^{(1)}\right\rangle + E_k^{(1)}\left\langle\psi_k^{(0)}\middle|\psi_k^{(0)}\right\rangle \tag{4.13}$$

The braket in the last term gives just unity since the eigenvectors are normalised. Furthermore, we can use the property that the Hamiltonian is an Hermitian operator to write

$$\left\langle\psi_k^{(0)}\middle|\hat{H}^{(0)}\psi_k^{(1)}\right\rangle = \left\langle\hat{H}^{(0)}\psi_k^{(0)}\middle|\psi_k^{(1)}\right\rangle = E_k^{(0)}\left\langle\psi_k^{(0)}\middle|\psi_k^{(1)}\right\rangle \tag{4.14}$$

and therefore we can express the relation in Eq. (4.13) as

$$E_k^{(0)}\left\langle\psi_k^{(0)}\middle|\psi_k^{(1)}\right\rangle + \left\langle\psi_k^{(0)}\middle|\hat{H}'\psi_k^{(0)}\right\rangle = E_k^{(0)}\left\langle\psi_k^{(0)}\middle|\psi_k^{(1)}\right\rangle + E_k^{(1)}\,, \tag{4.15}$$

which gives us the result for the **first-order corrections to the energy**

$$E_k^{(1)} = \left\langle\psi_k^{(0)}\middle|\hat{H}'\psi_k^{(0)}\right\rangle\,, \tag{4.16}$$

that is, the matrix element of the perturbed Hamiltonian evaluated by means of the unperturbed (original) eigenvectors. Note we since we know both the explicit expressions of the eigenvectors $\left|\psi_k^{(0)}\right\rangle$ and of $\hat{H}'$, we can always evaluate this quantity since we don't need to solve any equation before. We thus find that the **first-order correction to the energy** is the **expectation value of the Hamiltonian perturbation in the original states**.

Perturbative corrections to the infinite well potential. Let us illustrate this important result with an specific example. Assume that we have a particle confined to the infinite square well of width L. We have extensively studied this system in the present course, and at this point we probably know by heart the expression for its eigenfunctions and energies:

$$\psi_n^{(0)}(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)\,, \quad E_n^{(0)} = \frac{\pi^2 n^2\hbar^2}{2mL^2}\,, \quad n = 1, 2, 3, \ldots\,. \tag{4.17}$$

Consider now that we modify the original infinite potential well $V(x)$ with a sinusoidal correction of the form

$$\delta V(x) = \lambda V_1 \sin\left(\frac{\pi x}{L}\right) . \tag{4.18}$$

This correction has the same shape as the **ground state** of the system, and in particular vanishes at the edges of the well and has a maximum for $x = L/2$. In this perturbed potential, λ is some **dimensionless parameter**, while V_1 has units of energy and is responsible for the strength of the perturbation. For perturbation theory to work, λ must be small in some sense, and we will quantify below what this implies.

By means of Eq. (4.16), one can compute the first-order correction to the energy levels of this quantum state in terms of the following trigonometric integrals:

$$E_n^{(1)} = \left\langle \psi_n^{(0)} \middle| \hat{H}' \psi_n^{(0)} \right\rangle = \left\langle \psi_n^{(0)} \middle| V_1 \sin\left(\frac{\pi x}{L}\right) \psi_n^{(0)} \right\rangle = \frac{2V_1}{L} \int_0^L dx\, \sin^2\left(\frac{n\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) \tag{4.19}$$

By using known results for these trigonometric integrals, we can evaluate the first-order corrections to the first energy levels and find, in terms of strength of the perturbed potential V_1, and hence to obtain that at $\mathcal{O}(\lambda)$ in the perturbative expansion our estimate for the full energies of the system will be:

$$\begin{aligned}
E_1^{(1)} &= \frac{8V_1}{3\pi} \simeq 0.85\, V_1 \quad \to \quad E_1 = \frac{\pi^2\hbar^2}{2mL^2} + \lambda \frac{8V_1}{3\pi} , \\
E_2^{(1)} &= \frac{32V_1}{15\pi} \simeq 0.68\, V_1 \quad \to \quad E_2 = \frac{4\pi^2\hbar^2}{2mL^2} + \lambda \frac{32V_1}{15\pi} , \\
E_3^{(1)} &= \frac{72V_1}{35\pi} \simeq 0.66\, V_1 \quad \to \quad E_3 = \frac{9\pi^2\hbar^2}{2mL^2} + \lambda \frac{72V_1}{35\pi} .
\end{aligned} \tag{4.20}$$

You can evaluate the first-order perturbative corrections for higher excited states using the same approach.

At this point we are ready to answer an important question: in which respect λ is supposed to be small for perturbation theory to work? We have found that in this system, at first-order in the perturbative expansion, the energies of the eigenfunction are modified as

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \mathcal{O}\left(\lambda^2\right) = \frac{\pi^2 n^2 \hbar^2}{2mL^2} + \lambda F_n V_1 + \mathcal{O}\left(\lambda^2\right) , \tag{4.21}$$

with F_n being the numerical values defined above from the overlap integral,

$$F_n \equiv \frac{2}{L} \int_0^L dx\, \sin^2\left(\frac{n\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) = \mathcal{O}(1) , \tag{4.22}$$

Perturbative convergence criterion

For this perturbative expansion to make sense, the **first-order correction should be smaller than the unperturbed result**. Therefore, the **convergence condition** of the perturbative series is that

$$\frac{\lambda F_n V_1}{\pi^2 n^2 \hbar^2 / 2mL^2} \ll 1 \tag{4.23}$$

and therefore the condition that λ must satisfy to be considered **small** is

$$\lambda \ll \frac{\pi^2 n^2 \hbar^2}{2mL^2 F_n V_1} . \tag{4.24}$$

In particular, the stronger the size of the perturbed potential, V_1, the smaller than λ needs to be for the perturbative expansion to make sense. We also note that the **convergence condition** for the parameter λ depends on the principal quantum number n, and for very excited states the condition is less stringent than for the ground state. This makes sense, since we have seen that this potential induces approximately a constant correction to the energy levels irrespective of n but the unperturbed energy levels increase with n^2.

Finally, one can formally define the validity of the perturbative regime by the condition $\lambda = 1$, and in this case we have that

$$V_1 = \frac{\pi^2 n^2 \hbar^2}{2mL^2 F_k} \, . \tag{4.25}$$

For a given value of the principal quantum number n, if the strength of the perturbed potential V_1 is larger than this value then perturbation theory is completely unreliable and one needs to attempt to solve this problem by using other methods.

First-order corrections to the state vectors. Eq. (4.16) provided us with the result for the **first-order corrections to the energies**. We want now to evaluate the first-order correction to the state vectors using a similar strategy, and hence complete the first-order perturbative calculation for a general quantum system. The starting point will be the same relation that used for the calculation of the first-order corrections to the energies:

$$\hat{H}^{(0)}|\psi_n^{(1)}\rangle + \hat{H}'|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle \tag{4.26}$$

which can be also be expressed as

$$\left(\hat{H}^{(0)} - E_n^{(0)}\right)|\psi_n^{(1)}\rangle = \left(E_n^{(1)} - \hat{H}'\right)|\psi_n^{(0)}\rangle \, . \tag{4.27}$$

Note that the RHS of Eq. (4.27) is known, and formally what we are dealing with is a second-order inhomogeneous differential equation for $|\psi_n^{(1)}\rangle$.

Instead of trying to solve this equation directly, I will use the fact that the unperturbed eigenvectors form a **complete basis** in this Hilbert space, and thus I know for sure that I can expand $|\psi_n^{(1)}\rangle$ as a linear combination of the $\{|\psi_j^{(0)}\rangle\}$ in the usual manner:

$$|\psi_n^{(1)}\rangle = \sum_j c_j^{(n)}|\psi_j^{(0)}\rangle \, , \tag{4.28}$$

where we have explicitely indicated that for each value of the principal quantum number n we will have a different set of coefficients $\{c_j^{(n)}\}$. This way, we have transformed the problem of determining the correction to the quantum state $|\psi_n^{(1)}\rangle$ to that of finding the corresponding coefficients $c_j^{(n)}$ of its linear expansion.

If we insert this linear expansion into Eq. (4.27), we obtain

$$\left(\hat{H}^{(0)} - E_n^{(0)}\right)\left[\sum_j c_j^{(n)}|\psi_j^{(0)}\rangle\right] = \left(E_n^{(1)} - \hat{H}'\right)|\psi_n^{(0)}\rangle \, , \tag{4.29}$$

but we know how to evaluate the LHS, given that the $|\psi_j^{(0)}\rangle$ are the eigenvectors of the unperturbed Hamiltonian with eigenvalues $E_n^{(0)}$ and hence

$$\left(\hat{H}^{(0)} - E_n^{(0)}\right)\left[\sum_j c_j^{(n)}|\psi_j^{(0)}\rangle\right] = \sum_j c_j^{(n)}\left(\hat{H}^{(0)} - E_n^{(0)}\right)|\psi_j^{(0)}\rangle = \sum_j c_j^{(n)}\left(E_j^{(0)} - E_n^{(0)}\right)|\psi_j^{(0)}\rangle \, . \tag{4.30}$$

A crucial observation, as we will discover soon, is that the term $j = n$ does not contribute to the sum since then $\left(E_j^{(0)} - E_n^{(0)}\right) = 0$, and hence we can write

$$\left(\hat{H}^{(0)} - E_n^{(0)}\right)\left[\sum_j c_j^{(n)}|\psi_j^{(0)}\rangle\right] = \sum_{j\neq n} c_j^{(n)}\left(E_j^{(0)} - E_n^{(0)}\right)|\psi_j^{(0)}\rangle\,. \tag{4.31}$$

Taking this result into account, I find that Eq. (4.29) gives me:

$$\sum_{j\neq n} c_j^{(n)}\left(E_j^{(0)} - E_n^{(0)}\right)|\psi_j^{(0)}\rangle = \left(E_n^{(1)} - \hat{H}'\right)|\psi_n^{(0)}\rangle\,, \tag{4.32}$$

For reasons that will become obvious in a second, let me now multiply this expression from the left with the bra $\langle\psi_l^{(0)}|$, which gives me:

$$\sum_{j\neq n} c_j^{(n)}\left(E_j^{(0)} - E_n^{(0)}\right)\left\langle\psi_l^{(0)}\middle|\psi_j^{(0)}\right\rangle = \left\langle\psi_l^{(0)}\middle|\left(E_n^{(1)} - \hat{H}'\right)\psi_n^{(0)}\right\rangle. \tag{4.33}$$

Due to the orthonormality properties of the unperturbed eigenstates, the LHS will only be non-zero is $l = j$:

$$\sum_{j\neq n} c_j^{(n)}\left(E_j^{(0)} - E_n^{(0)}\right)\left\langle\psi_l^{(0)}\middle|\psi_j^{(0)}\right\rangle = \sum_{j\neq n} c_j^{(n)}\left(E_j^{(0)} - E_n^{(0)}\right)\delta_{lj} = c_l^{(n)}\left(E_l^{(0)} - E_n^{(0)}\right) \quad (l\neq n) \tag{4.34}$$

Using this result, Eq. (4.33) simplifies to

$$c_l^{(n)}\left(E_l^{(0)} - E_n^{(0)}\right) = \left\langle\psi_l^{(0)}\middle|\left(E_n^{(1)} - \hat{H}'\right)\psi_n^{(0)}\right\rangle = -\left\langle\psi_l^{(0)}\middle|\hat{H}'\psi_n^{(0)}\right\rangle \qquad (l\neq n)\,, \tag{4.35}$$

where in the last step we have used that $l \neq n$ and hence the term proportional to $E_n^{(1)}$ cancels out due to orthogonality.

But at this point we are basically done, since we have now determined the sought-for coefficients of the linear expansion of the first-order corrections to the state vectors defined in Eq. (4.28) as

$$c_l^{(n)} = \frac{\left\langle\psi_l^{(0)}\middle|\hat{H}'\psi_n^{(0)}\right\rangle}{E_n^{(0)} - E_l^{(0)}} \qquad (l\neq n)\,. \tag{4.36}$$

Note that we have all the information to evaluate them, since these are standard matrix elements of the perturbed Hamiltonian $\hat{H}'$ evaluated in the unperturbed states. Finally, we find that the **first-order corrections** to the state vectors are given by

$$|\psi_n^{(1)}\rangle = \sum_{j\neq n} c_j^{(n)}|\psi_j^{(0)}\rangle = \sum_{j\neq n}\frac{\left\langle\psi_j^{(0)}\middle|\hat{H}'\psi_n^{(0)}\right\rangle}{E_n^{(0)} - E_j^{(0)}}\left|\psi_j^{(0)}\right\rangle. \tag{4.37}$$

Note that in this expression the denominator is only non-zero (and hence the expression for $|\psi_n^{(1)}\rangle$ well defined) provided that the unperturbed spectrum is **non-degenerate**.

If instead the perturbed spectrum is degenerate, with two or more different eigenvectors $j \neq n$ sharing the same energy eigenvalue, $E_j^{(0)} = E_n^{(0)}$, then we are in trouble since the denominator will vanish for some elements of the sum rendering the calculation meaningless. We will discuss below how to tackle this situation, which will require the formulation of **degenerate perturbation theory**.

The perturbed infinite well revisited. Let me compute now the first-order perturbed wave functions corresponding to the perturbed infinite well potential that we considered above, and where the unperturbed results were given by Eq. (4.17). For simplicity, I will limit this calculation to the ground state, and hence what I need to compute is

$$|\psi_1^{(1)}\rangle = \sum_{j\neq 1} \frac{\left\langle \psi_j^{(0)} \middle| \hat{H}'\psi_1^{(0)} \right\rangle}{E_1^{(0)} - E_j^{(0)}} \left| \psi_j^{(0)} \right\rangle . \tag{4.38}$$

The energy difference is

$$E_1^{(0)} - E_j^{(0)} = \frac{\pi^2\hbar^2}{2mL^2} - \frac{\pi^2 j^2\hbar^2}{2mL^2} = -(j^2-1)\frac{\pi^2\hbar^2}{2mL^2} \tag{4.39}$$

and hence I can write, going back to the wavefunction notation which is more convenient to this problem,

$$\psi_1^{(1)}(x) = -\frac{2mL^2}{\pi^2\hbar^2}\sqrt{\frac{2}{L}}\sum_{j\neq 1}\frac{\left\langle \psi_j^{(0)} \middle| \hat{H}'\psi_1^{(0)} \right\rangle}{(j^2-1)} \sin\left(\frac{j\pi x}{L}\right) , \tag{4.40}$$

where I have moved all the prefactors outside the sum. The overlap integrals with the perturbed Hamiltonian are given by:

$$\left\langle \psi_j^{(0)} \middle| \hat{H}'\psi_1^{(0)} \right\rangle = \frac{2V_1}{L}\int_0^L dx \, \sin\left(\frac{j\pi x}{L}\right)\sin^2\left(\frac{\pi x}{L}\right) , \tag{4.41}$$

and these integrals can be computed, for example the first few terms in the sum give

$$\begin{aligned}
\left\langle \psi_2^{(0)} \middle| \hat{H}'\psi_1^{(0)} \right\rangle &= 0 \, , \\
\left\langle \psi_3^{(0)} \middle| \hat{H}'\psi_1^{(0)} \right\rangle &= -\frac{8}{15\pi}V_1 \, , \\
\left\langle \psi_4^{(0)} \middle| \hat{H}'\psi_1^{(0)} \right\rangle &= 0 \, , \\
\left\langle \psi_5^{(0)} \middle| \hat{H}'\psi_1^{(0)} \right\rangle &= -\frac{8}{105\pi}V_1 \, .
\end{aligned} \tag{4.42}$$

and hence we find that the first-order correction to the wave function of the ground state in this problem is given by:

$$\psi_1^{(1)}(x) = \frac{2mL^2V_1}{\pi^2\hbar^2}\sqrt{\frac{2}{L}}\left(\frac{1}{15\pi}\sin\left(\frac{3\pi x}{L}\right) + \frac{1}{3}\frac{1}{105\pi}\sin\left(\frac{5\pi x}{L}\right) + \ldots . \right) \tag{4.43}$$

If you represent graphically these results, you can verify that the sum over j converges rather quickly, and thus one does not need that many terms in order to produce a sensible estimate for $\psi_1^{(1)}(x)$.

4.1.2 Second-order perturbation theory

In the same manner, it is possible to compute the second-order corrections to the energy and to the eigenvectors (and eventually also at third order, then at fourth order, and so on). Let us show the explicit result for the second-order correction to the energy, $E_n^{(2)}$. The starting point will be Eq. (4.11),

$$\hat{H}^{(0)}\left|\psi_n^{(2)}\right\rangle + \hat{H}'\left|\psi_n^{(1)}\right\rangle = E_n^{(0)}\left|\psi_n^{(2)}\right\rangle + E_n^{(1)}\left|\psi_n^{(1)}\right\rangle + E_n^{(2)}\left|\psi_n^{(0)}\right\rangle m \tag{4.44}$$

and let me now multiply by the bra $\langle\psi_n^{(0)}|$ from the left:

$$\left\langle\psi_n^{(0)}\middle|\hat{H}^{(0)}\middle|\psi_n^{(2)}\right\rangle + \left\langle\psi_n^{(0)}\middle|\hat{H}'\middle|\psi_n^{(1)}\right\rangle = E_n^{(0)}\left\langle\psi_n^{(0)}\middle|\psi_n^{(2)}\right\rangle + E_n^{(1)}\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle + E_n^{(2)}\left\langle\psi_n^{(0)}\middle|\psi_n^{(0)}\right\rangle . \tag{4.45}$$

By exploiting the Hermiticity of $\hat{H}$, you can see how the first term in the LHS and in the RHS of the equation cancel with each other. Therefore we end up with the following relation

$$\left\langle \psi_n^{(0)} \middle| \hat{H}' \middle| \psi_n^{(1)} \right\rangle = E_n^{(1)} \left\langle \psi_n^{(0)} \middle| \psi_n^{(1)} \right\rangle + E_n^{(2)} \tag{4.46}$$

and hence the second-order correction to the unperturbed energies, $E_n^{(2)}$, is given by

$$E_n^{(2)} = \left\langle \psi_n^{(0)} \middle| \hat{H}' \middle| \psi_n^{(1)} \right\rangle - E_n^{(1)} \left\langle \psi_n^{(0)} \middle| \psi_n^{(1)} \right\rangle . \tag{4.47}$$

Crucially, the calculation of $E_n^{(2)}$ depends only on quantities that we have evaluated already, and hence it should be conceptually (though often not technically) straightforward to evaluate.

In particular, we can evaluate the matrix element $\left\langle \psi_n^{(0)} \middle| \psi_n^{(1)} \right\rangle$ based on the results we have obtained above in Eq. (4.37):

$$\left\langle \psi_n^{(0)} \middle| \psi_n^{(1)} \right\rangle = \left\langle \psi_n^{(0)} \middle| \sum_{j \neq n} \frac{\left\langle \psi_j^{(0)} \middle| \hat{H}' \psi_n^{(0)} \right\rangle}{E_n^{(0)} - E_j^{(0)}} \middle| \psi_j^{(0)} \right\rangle = 0 \tag{4.48}$$

since the only value of j which would make the matrix element non-zero, namely $j = n$, is not included in the sum. Therefore,

$$E_n^{(2)} = \left\langle \psi_n^{(0)} \middle| \hat{H}' \middle| \psi_n^{(1)} \right\rangle = \left\langle \psi_n^{(0)} \middle| \hat{H}' \sum_{j \neq n} \frac{\left\langle \psi_j^{(0)} \middle| \hat{H}' \psi_n^{(0)} \right\rangle}{E_n^{(0)} - E_j^{(0)}} \middle| \psi_j^{(0)} \right\rangle = \sum_{j \neq n} \frac{\left| \left\langle \psi_j^{(0)} \middle| \hat{H}' \psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_j^{(0)}} \tag{4.49}$$

is the sought-for result for the **second-order corrections to the energies**. Note that the overlap integrals are the same as those appearing in the first-order correction to the state vector, Eq. (4.37), and hence we should have evaluated them already!

The perturbed energies at $\mathcal{O}\left(\lambda^2\right)$

Putting together our calculations, we can express our estimate for the energy E_n of the full Hamiltonian of the problem up to second-order in the perturbative expansion as follows

$$E_n = E_n^{(0)} + \lambda \left\langle \psi_k^{(0)} \middle| \hat{H}' \psi_k^{(0)} \right\rangle + \lambda^2 \sum_{j \neq n} \frac{\left| \left\langle \psi_j^{(0)} \middle| \hat{H}' \psi_n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_j^{(0)}} + \mathcal{O}(\lambda^3) . \tag{4.50}$$

Interestingly, note that the fact that perturbation theory works at the first order does not guarantee that it will also work at the second order. For example, if we have a **quasi-continuum energy spectrum** with many values of $E_j^{(0)}$ very close to $E_n^{(0)}$, then the $\mathcal{O}\left(\lambda^2\right)$ correction may receive an enhancement that could spoil the convergence of the perturbative expansion.

4.2 Degenerate perturbation theory

The perturbation theory results that we have derived so far have assumed that the unperturbed system (defined by the original Hamiltonian $H^{(0)}$) is **non degenerate**, that is, that each eigenvector of the Hamiltonian has associated a distinct energy. If this is not the case, we quickly get into problems, as illustrated by the expression for the first-order corrections to the state vector Eq. (4.37), which diverges if the energy spectrum has some degeneracy (even a two-fold degeneracy makes the previous calculation unusable).

However, we know that many important quantum systems exhibit some level of energy degeneracy: for example, a particle in a two-dimensional box, the hydrogen atom (states with the same n but different values of l and m are degenerate), or the situation where we have two distinguishable particles confided into a one dimensional potential well. This situation demands to formulate an alternative approach to perturbation theory which works also if the unperturbed system exhibits a degenerate spectrum. We will develop this framework now, which we will denote as **degenerate perturbation theory**. First of all we will present the explicit calculation for the case of a two-fold degeneracy, and then explain how this calculation can be extended to an n-fold degeneracy.

Two-fold degeneracy. Let us start with a relatively simple quantum system, characterised by a unperturbed Hamiltonian $H^{(0)}$ with two orthonormal eigenvectors that share the same energy. This system is therefore defined by the following relations:

$$\hat{H}^{(0)}\big|\psi_a^{(0)}\big\rangle = E^{(0)}\big|\psi_a^{(0)}\big\rangle\,, \quad \hat{H}^{(0)}\big|\psi_b^{(0)}\big\rangle = E^{(0)}\big|\psi_b^{(0)}\big\rangle\,, \quad \big\langle\psi_b^{(0)}\big|\psi_a^{(0)}\big\rangle = 0\,. \tag{4.51}$$

We denote such situation as a **two-fold degeneracy**, given that we have two distinct eigenvalues which share the same energy.

An important property of this configuration is that **any linear combination of the two eigenvectors** is also an eigenvector of the Hamiltonian, with of course the same energy. That is, if we have a general linear combination given by

$$\big|\psi^{(0)}\big\rangle \equiv c_a\big|\psi_a^{(0)}\big\rangle + c_b\big|\psi_b^{(0)}\big\rangle\,, \tag{4.52}$$

with c_a, c_b being arbitrary complex coefficients, this state will also be an eigenstate of the original unperturbed Hamiltonian, given that

$$\hat{H}^{(0)}\big|\psi^{(0)}\big\rangle = \hat{H}^{(0)}\left(c_a\big|\psi_a^{(0)}\big\rangle + c_b\big|\psi_b^{(0)}\big\rangle\right) = c_aE^{(0)}\big|\psi_a^{(0)}\big\rangle + c_bE^{(0)}\big|\psi_b^{(0)}\big\rangle = E^{(0)}\big|\psi^{(0)}\big\rangle\,, \tag{4.53}$$

with the same value of the energy $E^{(0)}$ as the two eigenstates.

Assume now that we add a small perturbation to our Hamiltonian (small, since else perturbation theory would not be applicable), which we denote as

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}'\,, \tag{4.54}$$

where, as in the case of non-degenerate perturbation theory, we explicitely factorise the small dimensionless parameter λ (such that $\hat{H}'$ still has units of energy). In general, we will find that adding $\hat{H}'$ to the Hamiltonian of the system **breaks the degeneracy** of the unperturbed system, in that the perturbed energies associated to the perturbed states $\big|\psi_a\big\rangle$ and $\big|\psi_b\big\rangle$ will become different, $E_a \neq E_b$ once the $\mathcal{O}(\lambda)$ corrections have been calculated.

Conversely, if we start from the perturbed state vectors $\big|\psi_a\big\rangle$ and $\big|\psi_b\big\rangle$ and take the limit $\lambda \to 0$, we will have that $E_a, E_b \to E^{(0)}$ but in general the resulting state vectors in this limit will be **different** from the unperturbed eigenvectors $\big|\psi_a^{(0)}\big\rangle$ and $\big|\psi_b^{(0)}\big\rangle$, and will rather be a linear combination of them. This is not unexpected since any linear combination Eq. (4.52) represents an equally good eigenvector as our original choice in the presence of degeneracy, so we have some **intrinsic ambiguity**.

To make sense of perturbation theory, we need first of all to identify the linear combinations Eq. (4.52) to which the perturbed state vectors $\big|\psi_a\big\rangle$ and $\big|\psi_b\big\rangle$ reduce in the $\lambda \to 0$ limit - else I do not know with respect to what I am evaluating the perturbative correction.

Finding the degenerate unperturbed state vectors

We define the **degenerate unperturbed state vectors** $|\psi_1\rangle$ and $|\psi_2\rangle$ as those state vectors, eigenvectors of the unperturbed Hamiltonian $\hat{H}^0$, which are the $\lambda \to 0$ limit of the associated perturbed state vectors. In other words, we have that

$$\lim_{\lambda\to 0} |\psi_a\rangle = |\psi_1\rangle \qquad (\text{with energy } E_a \to E^{(0)})\,, \tag{4.55}$$

$$\lim_{\lambda\to 0} |\psi_b\rangle = |\psi_2\rangle \qquad (\text{with energy } E_b \neq E_a \to E^{(0)})\,, \tag{4.56}$$

where both $|\psi_1\rangle$ and $|\psi_2\rangle$ have associated energies $E^{(0)}$ and are constructed as linear combinations following the procedure of Eq. (4.52). These degenerate unperturbed state vectors are referred as "good" states in the textbook, which is perhaps not the most self-explanatory terminology that could be used.

Clearly, the applicability of degenerate perturbation theory requires first of all to determine what are these **degenerate unperturbed state vectors** to then subsequently evaluate their perturbative corrections. Let us illustrate this concept with a explicit example.

The perturbed harmonic oscillator in 2D. Let us consider here a quantum harmonic oscillator in two dimensions. The unperturbed Hamiltonian is given by

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \frac{1}{2}m\omega^2\left(x^2+y^2\right)\,. \tag{4.57}$$

We can now perturb this system by adding a small correction to the Hamiltonian,

$$\lambda\hat{H}' = \lambda m\omega^2 xy\,, \tag{4.58}$$

which induces as one can see a **coupling** between the oscillator modes in the x direction and those in the y direction, which in the regular 2D quantum harmonic oscillator are fully independent and can be treated separately as two 1D oscillators.

The ground state of the unperturbed system ($n_x = n_y = 0$) is non-degenerate and has energy $E = \hbar\omega$. However, the **first excited state** will be degenerate, since the two different eigenfunctions with ($n_x = 1, n_y = 0$) and ($n_x = 0, n_y = 1$) will have the same energy, $E = 2\hbar\omega$. Clearly, this is a situation for which non-degenerate perturbation theory breaks down.

One **possible basis** for these two degenerate states will be given by the product of the x-direction and y-direction wave functions with quantum numbers ($n_x = 1, n_y = 0$) and ($n_x = 0, n_y = 1$), namely

$$\psi_a^{(0)}(x,y) = \psi_0(x)\psi_1(y) = \sqrt{\frac{2}{\pi}}\frac{m\omega}{\hbar} y e^{-m\omega(x^2+y^2)/2\hbar}\,, \tag{4.59}$$

$$\psi_b^{(0)}(x,y) = \psi_1(x)\psi_0(y) = \sqrt{\frac{2}{\pi}}\frac{m\omega}{\hbar} x e^{-m\omega(x^2+y^2)/2\hbar}\,. \tag{4.60}$$

However, as mentioned above this is by no means a unique choice, and any pair of normalised orthogonal linear combinations

$$\psi_1^{(0)}(x,y) = c_a^{(1)}\psi_a^{(0)}(x,y) + c_b^{(1)}\psi_b^{(0)}(x,y)\,, \quad \psi_2^{(0)}(x,y) = c_a^{(2)}\psi_a^{(0)}(x,y) + c_b^{(2)}\psi_b^{(0)}(x,y)\,, \tag{4.61}$$

would represent an equally good basis, given that these linear combinations are also degenerate eigenstates of my Hamiltonian and have the **same energy** $E = 2\hbar\omega$. If we are to apply perturbation theory, we need to find the **degenerate unperturbed eigenfunctions**, that is, the combinations $\psi_1^{(0)}(x,y)$ and $\psi_2^{(0)}(x,y)$ which correspond to the $\lambda \to 0$ limit of the perturbed wavefunctions.

This example is particularly interesting in that the perturbed state can be **solved exactly** by rotating to a coordinate system such that

$$x' = \frac{x+y}{\sqrt{2}}\,, \quad y' = \frac{x-y}{\sqrt{2}}\,, \tag{4.62}$$

where you can show that the Hamiltonian is transformed as

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x'^2} + \frac{\partial^2}{\partial y'^2}\right) + \frac{1}{2}m(1+\lambda)\omega^2\left(x'\right)^2 + \frac{1}{2}m(1-\lambda)\omega^2\left(y'\right)^2\,. \tag{4.63}$$

which is of course nothing but two independent (decoupled) harmonic oscillators with the frequency $\omega_\pm = \omega\sqrt{1\pm\lambda}$. Here again we see that λ must be a small number: for $\lambda \geq 1$ the system stops even being a system of harmonic oscillators and becomes something completely different. This is another way of visualizing the **convergence criterion** of the perturbative expansion.

Expressing the perturbed Hamiltonian in this manner, it is clear that the **exact solutions** for the two-body system wave functions are

$$\psi_{nl}(x',y') = \psi_n^+(x')\psi_l^-(y')\,, \tag{4.64}$$

where ψ_n^+ is the n-th eigenfunction of a 1D harmonic oscillator with frequency $\omega_+ = \omega\sqrt{1+\lambda}$ and ψ_l^- is the l-th eigenfunction of a 1D harmonic oscillator with frequency $\omega_- = \omega\sqrt{1-\lambda}$. The energies associated to these exact solutions to the perturbed problem are given by:

$$E_{nl} = \hbar\omega_+\left(n+\frac{1}{2}\right) + \hbar\omega_-\left(l+\frac{1}{2}\right) = \hbar\omega\left(\sqrt{1+\lambda}\left(n+\frac{1}{2}\right) + \sqrt{1-\lambda}\left(l+\frac{1}{2}\right)\right)\,. \tag{4.65}$$

Crucially, we see that the exact energies of the perturbed problem are now **non-degenerate**: every independent combination of the quantum numbers n, l will have associated a different value of the energy E_{nl}. Furthermore, in the limit $\lambda \to 0$ we recover the original unperturbed quantum system and in this case the energies as we knew are degenerate, since

$$\lim_{\lambda\to 0} E_{nl} = \hbar\omega\left(n+l+1\right)\,, \tag{4.66}$$

and hence any combination of n and l for which $n+l$ is constant will be degenerate and will have associated the same energy.

In Fig. 4.1 we display the exact energies of the perturbed 2D harmonic oscillator problem, Eq. (4.65), as a function of the expansion parameter λ for two combinations of quantum numbers that lead to degenerate energies in the unperturbed Hamiltonian, namely $(n,l) = (4,1)$ and $(n,l) = (1,4)$ (left) and $(n,l) = (3,2)$ and $(n,l) = (2,3)$ (right). One can observe how in the $\lambda \to 0$ limit one recovers the degenerate unperturbed energies of Eq. (4.66), and how the perturbative correction breaks this degeneracy for $\lambda > 0$. Actually, note that beyond the first excited level of the system the degeneracy is larger than the two-fold one we are

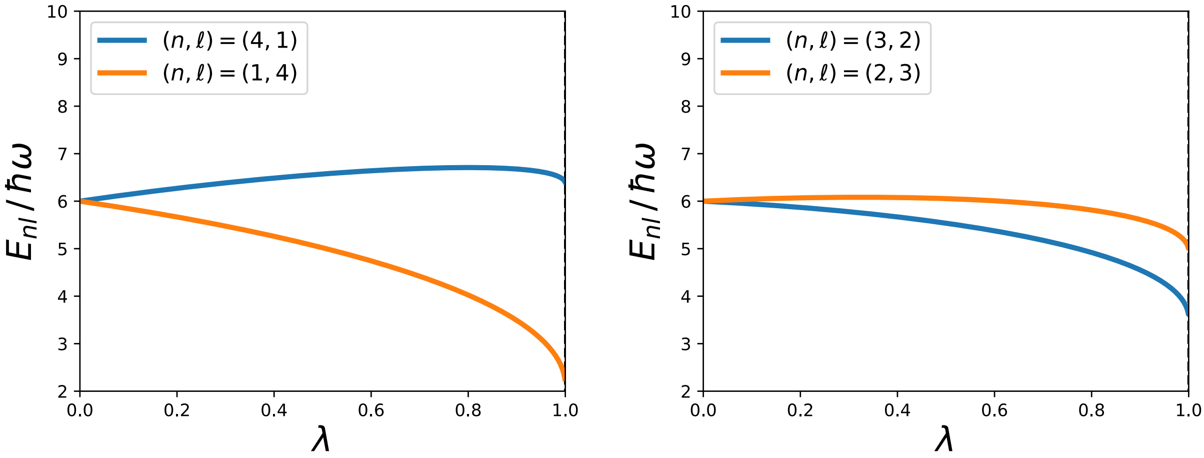

Figure 4.1: The exact energies of the perturbed 2D harmonic oscillator problem, Eq. (4.65), as a function of the expansion parameter λ for two combinations of quantum numbers that lead to degenerate energies in the unperturbed Hamiltonian, namely $(n,l)=(4,1)$ and $(n,l)=(1,4)$ (left) and $(n,l)=(3,2)$ and $(n,l)=(2,3)$ (right). One can observe how in the $\lambda \to 0$ limit one recovers the degenerate unperturbed energies of Eq. (4.66), and how the perturbative correction breaks this degeneracy for $\lambda > 0$.

interested here, so we will focus here only on the first excited state.

Since it this case we know what are the exact wave functions that solve the perturbed problem, Eq. (4.64), we can take the $\lambda \to 0$ limit and find the relevant **degenerate unperturbed eigenfunctions** to be used for the perturbative calculation of the energies. Rotating back to the original coordinate system (x,y), we obtain the following result:

$$\lim_{\lambda\to 0}\psi_{01}(x,y) = \lim_{\lambda\to 0}\psi_0^+\left(\frac{x+y}{\sqrt{2}}\right)\psi_1^-\left(\frac{x-y}{\sqrt{2}}\right) \tag{4.67}$$

$$= \sqrt{\frac{2}{\pi}\frac{m\omega}{\hbar}}\,\frac{x-y}{2}e^{-m\omega(x^2+y^2)/2\hbar} = \frac{1}{\sqrt{2}}\left(-\psi_a^{(0)}+\psi_b^{(0)}\right) \tag{4.68}$$

and likewise for the orthogonal combination:

$$\lim_{\lambda\to 0}\psi_{10}(x,y) = \frac{1}{\sqrt{2}}\left(\psi_a^{(0)}(x,y)+\psi_b^{(0)}(x,y)\right) \tag{4.69}$$

Therefore, we find that, for this specific problem, the “good” states of the unperturbed Hamiltonian, to be used in a perturbative calculation, are given by:

$$\psi_\pm^{(0)}(x,y) = \frac{1}{\sqrt{2}}\left(\psi_b^{(0)}(x,y)\pm\psi_a^{(0)}(x,y)\right)\,, \tag{4.70}$$

that is, these represent the $\lambda \to 0$ limit of the eigenstates of the **perturbed** Hamiltonian. Thus they are the correct baseline upon which to evaluate the perturbative corrections to the energy and the state vector of the system.

As will be shown below, if we know what are these “good” degenerate unperturbed eigenfunctions we can apply perturbation theory without the fear of obtaining unphysical results.

Degenerate perturbation theory. In general, we will not know in advance what are the suitable degenerate unperturbed eigenfunctions to be used in the perturbative calculation. For this reason, in the following we will keep the coefficients of the linear combination α and β as free parameters

$$\left|\psi^{(0)}\right\rangle = \alpha\left|\psi_a^{(0)}\right\rangle + \left|\beta\psi_b^{(0)}\right\rangle , \tag{4.71}$$

and show how we can determine their values from a direct calculation.

As in the case of non-degenerate perturbation theory, our goal is to take the perturbed Hamiltonian

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}' , \tag{4.72}$$

where λ is a small adimensional parameter, and express both the new state and the corresponding energies in terms of a **series expansion** in λ, starting from the original (unperturbed) values:

$$\begin{aligned} \left|\psi\right\rangle &= \left|\psi^{(0)}\right\rangle + \lambda\left|\psi^{(1)}\right\rangle + \lambda^2\left|\psi^{(2)}\right\rangle + \mathcal{O}\left(\lambda^3\right) , \\ E &= E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \mathcal{O}\left(\lambda^3\right) . \end{aligned} \tag{4.73}$$

Note that here we have suppressed the indices, since we are assuming the specific scenario of a **two-fold degeneracy** as mentioned above. While $E^{(0)}$ is degenerate, the perturbed Hamiltonian will break the degeneracy and we will obtain two distinct solutions for the perturbed energy E.

We can now insert the series expansions in λ in the Schroedinger equation, expand and collect terms that are proportional to the same power of the expansion parameter λ. The first non-trivial relation that we find is the one that determines the **first-order corrections to the energy**, that is

$$\hat{H}^{(0)}\left|\psi^{(1)}\right\rangle + \hat{H}'\left|\psi^{(0)}\right\rangle = E^{(0)}\left|\psi^{(1)}\right\rangle + E^{(1)}\left|\psi^{(1)}\right\rangle , \tag{4.74}$$

which is nothing but the same equation we had in the non-degenerate case, Eq. (4.12). Now, as opposed to the case of non-degenerate perturbation theory, we will multiply this expression from the left with the bra $\left\langle\psi_a^{(0)}\right|$ instead of by the original unperturbed eigenvector $\left\langle\psi^{(0)}\right|$ (for the reason that we don't even really know how to select $\left\langle\psi^{(0)}\right|$ at this point!)

By doing this, we end up with the following expression

$$\left\langle\psi_a^{(0)}\middle|\hat{H}^{(0)}\psi^{(1)}\right\rangle + \left\langle\psi_a^{(0)}\middle|\hat{H}'\psi^{(0)}\right\rangle = E^{(0)}\left\langle\psi_a^{(0)}\middle|\psi^{(1)}\right\rangle + E^{(1)}\left\langle\psi_a^{(0)}\middle|\psi^{(0)}\right\rangle \tag{4.75}$$

Now using the Hermiticity of $\hat{H}^{(0)}$, and introducing the expansion that defines the "good" eigenvectors (which remember, we are trying to determine here),

$$\left|\psi^{(0)}\right\rangle = \alpha\left|\psi_a^{(0)}\right\rangle + \beta\left|\psi_b^{(0)}\right\rangle , \tag{4.76}$$

we end up with the following result:

$$\alpha\left\langle\psi_a^{(0)}\middle|\hat{H}'\psi_a^{(0)}\right\rangle + \beta\left\langle\psi_a^{(0)}\middle|\hat{H}'\psi_b^{(0)}\right\rangle = \alpha E^{(1)} \tag{4.77}$$

This result can be express in a more compact manner in terms of the **matrix elements** of the perturbed Hamiltonian, defined as

$$W_{ij} \equiv \alpha\left\langle\psi_i^{(0)}\middle|\hat{H}'\psi_j^{(0)}\right\rangle , \quad i,j = a,b . \tag{4.78}$$

Taking into account this definition, and repeating the calculation now multiplying Eq. (4.12) from the left with the bra $\langle\psi_b^{(0)}|$, we end up with the following **matrix equation**:

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} , \tag{4.79}$$

which is nothing but the **eigenvalue equation** for the matrix **W**. By solving this eigenvalue equation we obtain both the first-order perturbative corrections to the energy, $E^{(1)}$ and well as the eigenvectors α and β which define the "good" states of the unperturbed Hamiltonian. Note that as expected we will have two solutions for $E^{(1)}$ and two for the vector (α, β) which will define the two sought-for "good" combinations.

The solution of this eigenvalue equation is provided by the **characteristic equation** of the eigenvalue problem, given by

$$\begin{vmatrix} W_{aa} - E^{(1)} & W_{ab} \\ W_{ba} & W_{bb} - E^{(1)} \end{vmatrix} = 0 \tag{4.80}$$

If we use that the matrix elements satisfy $W_{ba} = W_{ab}^*$ (because of the hermiticity of the Hamiltonian), then we find that the solutions of the resulting quadratic equation will be given as follows:

$$E_\pm^{(1)} = \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2}\right] . \tag{4.81}$$

Again, recall that W_{aa} and W_{bb} are real because of hermiticity. Hence, provided we evaluate the matrix elements W_{ij}, we should able to evaluate the first order corrections to the energy and to determine the "good" states of the unperturbed Hamiltonian.

Degenerate perturbation theory

Eq. (4.81) is the fundamental results of two-fold degenerate perturbation theory: the two roots correspond to the two perturbed energies $E_\pm^{(1)}$. We hence see how the perturbed Hamiltonian **lifts the degeneracy** which is present at the unperturbed level. Note also that in the case where $W_{ab} = 0$ then the eigenvalues are trivially

$$E_+^{(1)} = W_{aa} = \left\langle \psi_a^{(0)} \middle| \hat{H}' \psi_a^{(0)} \right\rangle , \qquad E_+^{(2)} = W_{bb} = \left\langle \psi_b^{(0)} \middle| \hat{H}' \psi_b^{(0)} \right\rangle \tag{4.82}$$

which is the result obtained using **non-degenerate perturbation theory**, Eq. (4.16).

Clearly, if we can start from the "good" states of the unperturbed Hamiltonian, then we would have a nice head start since we could directly use non-degenerate perturbative calculations.

The perturbed 2D harmonic oscillator reloaded. Let us verify that these findings are consistent with our previous calculation for the perturbed 2D harmonic oscillator. To do this, we need to evaluate the matrix elements W_{ij} and then solve the corresponding eigenvalue equation. You can convince yourselves that

$$W_{aa} = \int\int \psi_a^{(0)}(x,y)\hat{H}'\psi_a^{(0)}(x,y)dxdy = \omega^2 \int dx\, x\, |\psi_0(x)|^2 \int dy\, y\, |\psi_0(y)|^2 = 0 \tag{4.83}$$

since the ground state wave functions are symmetric in their argument. For the same reasoning, $W_{bb} = 0$. The only non-trivial matrix element is the off-diagonal one:

$$W_{aa} = \int\int \psi_a^{(0)}(x,y)\hat{H}'\psi_b^{(0)}(x,y)dxdy = \omega^2 \int dx\, x\, \psi_0(x)\psi_1(x) \int dy\, y\, \psi_0(y)\psi_1(y) = \frac{\hbar\omega}{2}\,, \tag{4.84}$$

which can be evaluated for example using the explicit one-particle wave functions of the unperturbed Harmonic oscillator problem.

Hence the matrix which is to be diagonalised turns out to be

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} = \frac{\hbar\omega}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\,, \tag{4.85}$$

which can be easily diagonalised and whose eigenvalues and eigenvectors turn out to be

$$|\psi_\pm^{(0)}\rangle = \frac{1}{\sqrt{2}}\left(|\psi_a^{(0)}\rangle \pm |\psi_b^{(0)}\rangle\right) \tag{4.86}$$

$$E_\pm^{(1)} = \pm\frac{\hbar\omega}{2}\,, \tag{4.87}$$

consistently with the results that we found before with the full analytic solution to this problem. To see this, take the exact solution for the energies, Eq. (4.65), and expand for the first order in λ:

$$\begin{aligned} E_{nl} &= \hbar\omega\left(\sqrt{1+\lambda}\left(n+\frac{1}{2}\right) + \sqrt{1-\lambda}\left(l+\frac{1}{2}\right)\right)\,. \\ &\simeq \hbar\omega\left(\left(1+\frac{\lambda}{2}\right)\left(n+\frac{1}{2}\right) + \left(1-\frac{\lambda}{2}\right)\left(l+\frac{1}{2}\right)\right) = \hbar\omega(n+l+1) + \lambda\hbar\omega\frac{(n-l)}{2}\,. \end{aligned} \tag{4.88}$$

Now, here we were considering the two-fold degeneracy associated to $(n,l) = (1,0)$ and $(n,l) = (0,1)$, so the correction is

$$\delta E = \lambda \times \left(\pm\frac{\hbar\omega}{2}\right)\,, \tag{4.89}$$

exactly as we wanted to demonstrate.

The "good" states theorem

A systematic strategy to find the "good" states to be used in degenerate perturbation theory applications is the following. Consider an hermitian operator $\hat{A}$ such that $\left[\hat{A},\hat{H}^{(0)}\right] = \left[\hat{A},\hat{H}'\right] = 0$. This operator is such that the degenerate eigenvectors of $\hat{H}^{(0)}$, namely $|\psi_a^{(0)}\rangle$ and $|\psi_b^{(0)}\rangle$ are also eigenvectors of this operator, but this time with distinct eigenvalues, that is

$$\hat{A}|\psi_a^{(0)}\rangle = \mu|\psi_a^{(0)}\rangle\,, \quad \hat{A}|\psi_b^{(0)}\rangle = \nu|\psi_b^{(0)}\rangle \qquad \mu \neq \nu\,. \tag{4.90}$$

Then $|\psi_a^{(0)}\rangle$ and $|\psi_b^{(0)}\rangle$ correspond to the **"good" states** to be used in the perturbative calculation.

Generalisation to higher order degeneracy. The previous derivation can be generalised to deal with an n-fold degeneracy using the same strategy. For example, let us consider the case of the **three-fold degeneracy**. Consider we have an unperturbed Hamiltonian $\hat{H}^{(0)}$ with three eigenvectors with identical energy, say $\left|\psi_a^{(0)}\right\rangle$, $\left|\psi_b^{(0)}\right\rangle$, and $\left|\psi_c^{(0)}\right\rangle$. To determine the first-order perturbative corrections to the unperturbed energy $E^{(0)}$, we need to evaluate the matrix elements of the perturbed Hamiltonian

$$W_{ij} \equiv \left\langle \psi_i^{(0)} \middle| \hat{H}' \psi_j^{(0)} \right\rangle , \quad i,j = a,b,c\,, \tag{4.91}$$

and then solve the corresponding **eigenvalue equation**:

$$\begin{pmatrix} W_{aa} & W_{ab} & W_{ac} \\ W_{ba} & W_{bb} & W_{bc} \\ W_{ca} & W_{cb} & W_{cc} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} = E^{(1)} \begin{pmatrix} \alpha \\ \beta \\ \gamma \end{pmatrix} . \tag{4.92}$$

to determine the “good
states of the unperturbed Hamiltonian, defined in terms of the linear combination

$$|\psi^{(0)}\Big\rangle = \alpha|\psi_a^{(0)}\Big\rangle + \beta|\psi_b^{(0)}\Big\rangle + \gamma|\psi_c^{(0)}\Big\rangle \tag{4.93}$$

The same method generalizes to the case of an **n-fold degeneracy**.

4.3 The fine structure of hydrogen

We now have the tools to deploy perturbation theory to quantify the **fine structure** of the hydrogen atom. By this term, we refer to a number of subleading effects that modify the energy levels and the wave functions of the electron in the hydrogen atom with respect to those that were computed in Sect. 2.3, and that are referred as the **Bohr energy levels**:

$$E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2} = -\frac{13.6\,\text{eV}}{n^2}\,, \tag{4.94}$$

where -13.6 eV indicate the ionisation energy of hydrogen. These corrections are numerically subleading but highly relevant for many applications in atomic physics, which require a precise prediction for the energy levels of the hydrogen atom.

This fine structure of the hydrogen atom is composed by two effects, both of which are suppressed by a factor α^2 as compared to the Bohr energies, where the **fine structure constant**, the fundamental parameter of the quantum theory of electromagnetism, is a **dimensionless parameter** defined as

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137.036}\,. \tag{4.95}$$

Note that in terms of the fine structure constant α, the Bohr energy levels of the hydrogen atom are given by

$$E_n = -\frac{\alpha^2 m_e c^2}{2n^2}\,, \tag{4.96}$$

and as we will show below, the effects that will evaluate now scale as $E^{(1)} = \mathcal{O}(\alpha^4)$.

The two component of this **fine structure** of the hydrogen atom are:

- The **relativistic correction**, which accounts for the the fact that electrons move at energies not that far from the speed of light, and therefore one needs to consider special relativity effects.
- The **spin-orbit coupling**, which accounts for the interaction of the electron spin with its orbital motion

(technically, with the magnetic field generated by the proton which “orbits” around the electron from the viewpoint of the latter).

Here we will discuss these two components of the fine structure in turn. There exist even smaller corrections, such as the **Lamb shift** and the **hyperfine structure**, but we will not consider them in this course.

4.3.1 The relativistic correction

Let us start by the Hamiltonian of the hydrogen atom:

$$\hat{H}\psi(\mathbf{r}) = \left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{e^2}{4\pi\epsilon_0 r}\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})\,. \tag{4.97}$$

The first term in the Hamiltonian corresponds to the operator representation of the classical **kinetic energy** T. However, if the electron moves at a non-negligible fraction of the speed of light c, the classical expression for the kinetic energy will not be accurate and one instead should use the corresponding relativistic expression:

$$T_{\rm rel} = mc^2\left(\gamma - 1\right)\,, \tag{4.98}$$

where we have used the usual **dilation factor** defined in relativistic calculations

$$\gamma = \frac{1}{\sqrt{1-\beta^2}}\,, \quad \beta \equiv \frac{v}{c}\,. \tag{4.99}$$

We can estimate the relevance of relativistic effects of the electron in the hydrogen atom as follows. For an **electron in the ground state**, its kinetic energy is of the order of $T = \mathcal{O}(10)$ eV (recall that the ionisation energy is 13.6 eV). The ratio of kinetic over rest mass then determines the dilation factor

$$\frac{T_{\rm rel}}{E_{\rm rest}} = \frac{10\ {\rm eV}}{0.511\ {\rm MeV}} = \gamma - 1\,, \tag{4.100}$$

where we have entered the value of the rest mass energy of the electron. One then finds that $\beta \simeq 0.006$, hence the electron moves at a speed of **0.6% the speed of light**: enough for its relativistic correction to be measurable.

In order to find the operator representation of $T_{\rm rel}$, and hence determine what are the relativistic corrections to the Hamiltonian of the hydrogen atom, we need to express $T_{\rm rel}$ in terms of the linear momentum. Taking into account that in special relativity the total energy of a particle is the sum of its kinetic and rest energies, you can find that the corresponding expression is

$$T_{\rm rel} = mc^2\left[\sqrt{1+\left(\frac{p}{mc}\right)^2} - 1\right] \simeq \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \mathcal{O}\left(\frac{p^6}{m^5c^4}\right)\,. \tag{4.101}$$

It is perfectly fine to truncate this Taylor expansion at the first order: the expansion parameter is p/mc, and for an electron in the hydrogen atom this is a small number as demonstrated above: it is the ratio of its kinetic energy to its rest mass. Another way to see why this is the relevant expansion parameter is to express the previous equation as

$$T_{\rm rel} = \frac{p^2}{2m} \times \left(1 - \frac{p^2}{4m^2c^2} + \mathcal{O}\left(\frac{p^4}{m^4c^4}\right)\right)\,. \tag{4.102}$$

Henceforth, at first order in perturbation theory, the lowest-order **relativistic correction** to the Hamiltonian of the hydrogen atom is given by:

$$H_r' = -\frac{p^4}{8m^3c^2}\,. \tag{4.103}$$

We can thus now use **perturbation theory**, Eq. (4.16), to determine the first order corrections to the Bohr energies:

$$E_r^{(1)} = \langle H_r' \rangle = -\frac{1}{8m^3c^2}\left\langle \psi_n^{(0)} \middle| \hat{p}^4 \psi_n^{(0)} \right\rangle = -\frac{1}{8m^3c^2}\left\langle \hat{p}^2\psi_n^{(0)} \middle| \hat{p}^2 \psi_n^{(0)} \right\rangle . \tag{4.104}$$

Note that the size of the perturbative correction will depend (at least) on the principal quantum number n. In order to make progress with our calculation, we can use the fact that the Schroedinger equation for the unperturbed states of the hydrogen atom reads

$$\hat{p}^2\left|\psi_n^{(0)}\right\rangle = 2m\left(E_n - V(r)\right)\left|\psi_n^{(0)}\right\rangle \tag{4.105}$$

to evaluate the first order correction in the following manner:

$$E_r^{(1)} = -\frac{1}{2mc^2}\left\langle (E_n - V(r))^2 \right\rangle = -\frac{1}{2mc^2}\left[E_n^2 - 2E_n\langle V\rangle + \left\langle V^2\right\rangle\right]\,, \tag{4.106}$$

which by inserting the **Coulomb potential** gives the following result:

$$E_r^{(1)} = -\frac{1}{2mc^2}\left[E_n^2 - \frac{E_n e}{2\pi\epsilon_0}\left\langle\frac{1}{r}\right\rangle + \frac{e^2}{16\pi^2\epsilon_0^2}\left\langle\frac{1}{r^2}\right\rangle\right] \tag{4.107}$$

By using the radial probability distribution $P_{nl}(r) = r^2|R_{nl}(r)|^2$ associated to the unperturbed electronic orbital $\psi_{nlm}(r,\theta,\phi)$, we can evaluate these expectation values

$$\left\langle\frac{1}{r}\right\rangle = \int_0^\infty dr\, r|R_{nl}(r)|^2 = \frac{1}{n^2a}\,, \tag{4.108}$$

$$\left\langle\frac{1}{r^2}\right\rangle = \int_0^\infty dr\, |R_{nl}(r)|^2 = \frac{1}{(\ell+1/2)\, n^3a^2}\,, \tag{4.109}$$

in terms of the Bohr radius a. We can insert these results in Eq. (4.107) and express the result in terms of the unperturbed energy $E_n^{(0)}$. The final result for the **relativistic correction** to the Bohr energy levels of the hydrogen atom is

$$E_r^{(1)} = -\frac{1}{2m_ec^2}\left(E_n^{(0)}\right)^2\left[\frac{4n}{\ell+1/2} - 3\right] = -\frac{1}{2m_ec^2}\left(\frac{\alpha^2m_ec^2}{2n^2}\right)^2\left[\frac{4n}{\ell+1/2} - 3\right]\,, \tag{4.110}$$

which can be simplified to read:

$$E_r^{(1)} = -\frac{\alpha^4m_ec^2}{8n^4}\left[\frac{4n}{\ell+1/2} - 3\right]\,, \tag{4.111}$$

which as discussed before is a correction of the order of $\mathcal{O}(E_r^{(1)}) = \alpha^4mc^2$.

A few comments on this interesting results are in order:

- The use of perturbation theory appears to be **fully justified**: the **relative correction** due to relativistic effects is proportional to the ratio between the unperturbed (non relativistic) energy and the rest energy of the electron

  $$\frac{E_r^{(1)}}{E_n^{(0)}} \propto \frac{E_n^{(0)}}{mc^2} \simeq 2\times10^{-5}\,. \tag{4.112}$$

  Clearly, the next term in the perturbative expansion should be of the order $\mathcal{O}\left(10^{-10}\right)$ and hence it is perfectly fine to just keep the leading term.

- In the unperturbed hydrogen atom, electronic orbitals are **degenerate**: all the states ψ_{nlm} with common values of the principal number n and different ℓ and m share the same energy $E_n^{(0)}$.

  This degeneracy is **partially lifted** by the relativistic correction, and now at first order in perturbation theory the energies of the electronic orbitals of the hydrogen atom $E_{n,\ell}$ depend both on n and ℓ:

  $$E_{n,\ell} = -\frac{\alpha^2 m_e c^2}{2n^2} - \frac{\alpha^4 m_e c^2}{8n^4}\left[\frac{4n}{\ell+1/2} - 3\right] = -\frac{\alpha^2 m_e c^2}{2n^2}\left(1 + \frac{\alpha^2}{4n^2}\left[\frac{4n}{\ell+1/2} - 3\right]\right) . \tag{4.113}$$

  Note however that the $(2\ell+1)$-fold degeneracy in m remains and it is not affected by the relativistic correction.

- As a related point, one might have argued that the use of **non-degenerate perturbation theory** was not appropriate since, well, the electronic orbitals of the unperturbed hydrogen atom are **degenerate**. Fortunately, ψ_{nlm} can be shown to be "good" states for this problem, due to the rotationally symmetric nature of the perturbation, which depends only on r but not on θ and ϕ, as indicated by Eq. (4.107).

4.3.2 The spin-orbit coupling interaction

The second contribution to the fine structure of hydrogen, in addition to the relativistic correction, comes from the interaction of the **electron spin** with its own **orbital motion**. Recall from your electromagnetism courses that any orbiting electric charge generates a magnetic field $\mathbf{B}$. From the viewpoint of the electron, the positive charge of the proton **orbiting around it** is generating an "external" magnetic field which will interact with its spin.

Indeed, this magnetic field generated by the proton "orbital motion" will interact with the **magnetic dipole moment of the electron** that arises from its spin, leading to the Hamiltonian

$$H = -\mathbf{B}\cdot\boldsymbol{\mu} , \tag{4.114}$$

which tends to orient the spin of the electron in the same direction as its magnetic field (since this is the configuration that minimises the total energy of the system). We denote this effect as the **spin-orbit coupling** or interaction, and here we will compute how it modifies the unperturbed (Bohr) energies of the hydrogen atom. Since electrons orbiting in different directions and with spin pointing in different orientations will receive a different contribution from this perturbed Hamiltonian, we can expect that this spin orbit coupling **breaks further the degeneracy** present in the electronic orbitals of the hydrogen atom.

In order to construct the perturbed Hamiltonian responsible for the spin orbit interaction, we need to evaluate the magnetic dipole moment of the electron and the magnetic field generated by the proton. The calculation involves some interesting elements of classical electrodynamics combined with some corrections which are beyond the scope of this course, for example, the electron magnetic moment $\boldsymbol{\mu}_e$ can only be computed in a proper way in relativistic quantum mechanics, that is in **quantum field theory**, and the result is

$$\boldsymbol{\mu}_e = -\frac{e}{m}\boldsymbol{S} , \tag{4.115}$$

with $\boldsymbol{S}$ being the electron spin. Here we just quote the final result for the Hamiltonian responsible for this spin-orbit interaction in terms of $\boldsymbol{S}$ and the angular momentum $\boldsymbol{L}$:

$$H'_{\rm so} = \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2r^3}\boldsymbol{S}\cdot\boldsymbol{L} , \tag{4.116}$$

where $\boldsymbol{L}$ is the angular momentum associated to the orbital motion of the proton around the electron, from the electron perspective. We can now use our perturbation theory toolbox to evaluate how this perturbed Hamiltonian modifies the Bohr energy levels of the hydrogen atom.

Adding the spin-orbit correction Eq. (4.116) to the unperturbed Hamiltonian of the hydrogen atom has an important consequence: the Hamiltonian no longer commutes with $\boldsymbol{L}$ and $\boldsymbol{S}$ separately, so spin and orbital angular momentum are **no longer conserved separately**. However, $H'_{\rm so}$ does commute with the total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$, so we can write

$$\left[\hat{H}'_{\rm so}, \boldsymbol{J}\right] = \left[\hat{H}'_{\rm so}, \hat{L}^2\right] = \left[\hat{H}'_{\rm so}, \hat{S}^2\right] = 0\,. \tag{4.117}$$

By recalling the generalised Ehrenfest theorem, hence we know that $\boldsymbol{J}$, S^2 and L^2 will be conserved quantities not affected by the spin-orbit interaction. This implies that once one accounts for spin-orbit coupling effects, one needs to change the quantum numbers that label the eigenstates of the full Hamiltonian as follows:

- **Unperturbed Hamiltonian** H^0: the eigenstates of the Hamiltonian can be constructed from the eigenstates of $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, $\hat{S}_z$.
- **Perturbed Hamiltonian** $H = H^0 + H'_{\rm so}$: the eigenstates of the Hamiltonian can be constructed from the eigenstates of $\hat{J}^2$, $\hat{J}_z$, $\hat{S}^2$, $\hat{L}^2$. So we have four quantum numbers as well, just they are different as compared to those in the unperturbed case.

Let us use this property to determine the sought-for first-order corrections to the energy levels of the hydrogen atom due to the spin-orbit interactions. First of all let us express $H'_{\rm so}$ in terms of those quantities that are conserved upon this interaction. We can write

$$J^2 = (\boldsymbol{L} + \boldsymbol{S})^2 = L^2 + S^2 + 2\boldsymbol{S}\cdot\boldsymbol{L}\,, \tag{4.118}$$

which implies that the spin-orbit coupling Hamiltonian will be proportional to:

$$\boldsymbol{S}\cdot\boldsymbol{L} = \frac{1}{2}\left(J^2 - L^2 - S^2\right) \tag{4.119}$$

Now, as we said before, the eigenstates of $\hat{H} = \hat{H}^0 + \hat{H}'_{\rm so}$ can be labelled by the following conserved quantum numbers

$$|n, l, s, j, m_j\rangle\,, \tag{4.120}$$

where m_j is the quantum number associated to J_z. Applying the $\boldsymbol{S}\cdot\boldsymbol{L}$ operator to these eigenstates returns

$$\boldsymbol{S}\cdot\boldsymbol{L}|n, l, s, j, m_j\rangle = \frac{1}{2}\left(J^2 - L^2 - S^2\right)|n, l, s, j, m_j\rangle = \frac{\hbar^2}{2}\left(j(j+1) - \ell(\ell+1) - s(s+1)\right)|n, l, s, j, m_j\rangle \tag{4.121}$$

so using that $s = 1/2$ we conclude that the eigenstates of the operator $\boldsymbol{S}\cdot\boldsymbol{L}$ are

$$\frac{\hbar^2}{2}\left(j(j+1) - \ell(\ell+1) - \frac{3}{4}\right)\,. \tag{4.122}$$

We are now ready to compute the expectation values of the perturbed Hamiltonian. By using non-degenerate perturbation theory (for the same reason as in the case of the relativistic correction), we can use that

$$E^{(1)}_{\rm so} = \langle H'_{\rm so}\rangle = \left(\frac{e^2}{8\pi\epsilon_0}\right)\frac{1}{m^2c^2}\left\langle\frac{\boldsymbol{S}\cdot\boldsymbol{L}}{r^3}\right\rangle \tag{4.123}$$

These perturbed eigenstates have well-defined values of $\langle \boldsymbol{S} \cdot \boldsymbol{L} \rangle$ computed above. Recall that in the hydrogen atom, the dependence of the wave function on the radial coordinate r **factorises** with the dependence on the angular variables (θ, ϕ) and the spin, and hence expectation values can be computed separately. By using the result of the expectation value of r^{-3}

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{\ell(\ell+1/2)(\ell+1)n^3a^3} \tag{4.124}$$

we end up with the following result

$$E_{\rm so}^{(1)} = \frac{e^2\hbar}{16\pi\epsilon_0 m^2c^2}\frac{(j(j+1)-\ell(\ell+1)-3/4)}{\ell(\ell+1/2)(\ell+1)n^3a^3} = \frac{\left(E_n^{(0)}\right)^2}{mc^2}\left[\frac{n\,(j(j+1)-\ell(\ell+1)-3/4)}{\ell(\ell+1/2)(\ell+1)}\right] \,, \tag{4.125}$$

and hence it is of the relative order, $\mathcal{O}\left(E_n^{(0)}/mc^2\right)$, sams as in the case of the relativistic correction. Note that Eq. (4.125) can be applied only to states with $\ell > 0$, since those for $\ell = 0$ have vanishing angular momentum and hence they do not experience the effects of the spin-orbit coupling.

Combining the relativistic correction with the spin-orbit correction, we end up with the following result for the **fine structure** of the hydrogen atom:

$$E_{\rm fs}^{(1)} = \frac{\left(E_n^{(0)}\right)^2}{2mc^2}\left(3 - \frac{4n}{j+1/2}\right) \tag{4.126}$$

and the final result for the energies of the electronic orbitals of the hydrogen atom at $\mathcal{O}\left(\alpha^2\right)$ in perturbation theory are given by the following result:

$$E_{nj} = -\frac{(13.6\,\text{eV})}{n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+1/2} - \frac{3}{4}\right)\right] \,. \tag{4.127}$$

Some comments about this foundational calculation:

- The *relative effect* of the fine-structure corrections is most important for the ground state of hydrogen $(n = 1)$, and then decreases as $1/n$.
- Likewise, the higher the value of the total angular momentum j, the less important the relative impact of the fine structure effects: for a given n, these corrections are the largest for $j = 1/2$.
- The degeneracy in ℓ is now broken but there is still **degeneracy in j:** all states with the same total angular momentum j will exhibit the same energy.
- The "good" quantum numbers to describe the electronic orbitals of the hydrogen atom are now n, ℓ, s, j, m_j, to be compared to those we used for the unperturbed orbitals: n, ℓ, s, m_ℓ, m_s.

Interestingly, let me point out that the **exact expression** for the fine structure of hydrogen can be derived from the Dirac equation that describes the relativistic quantum mechanics of fermions, it can be checked that expanding this exact result up to $\mathcal{O}\left(\alpha^2\right)$.

Summary

We can now recapitulate what have we learned in this chapter concerning the application of perturbation theory to quantum systems for which a closed form analytic solution of the corresponding Schroedinger equation does not exist.

I/ In the case of non-degenerate energy spectra, perturbation theory provides a systematic prescription to improve our estimate of the energies and state vectors of the system in the case of a modified Hamiltonian.

II/ This perturbative expansion is controlled by some small expansion parameter, which sets the convergence rate (or lack thereof) of this expansion.

III/ The perturbation theory method applied also to systems for which the exact solution is known, and verify that the correct expressions are obtained in terms of the power series expansion in the small parameter λ.

IV/ The presence of degenerate energy states can spoil the convergence of perturbation theory, unless we rotate the unperturbed states to a special basis where this problem is absent.

V/ Perturbation theory often breaks the degeneracies that affect the energy spectra of unperturbed systems, since they affect different unperturbed eigenvectors in a different manner.

VI/ Using perturbation theory we can evaluate the first non-trivial corrections to the Bohr energy levels of the hydrogen atom, which correspond to $\mathcal{O}\left(\alpha^2\right)$ terms in terms if the fine structure constant.