9 Perturbation theory

9.1 Time-independent perturbation theory

Time-independent means we assume that the Hamiltonian H does not depend on time. Then, to solve the Schrödinger equation, we must determine the eigenvalues and eigenvectors of H. In most physical situations no exact solution to the eigenvalue problem of the Hamiltonian H is known. Actually, exactly solvable situations are the exception. But it often happens that the Hamiltonian H can be written as $H = H_0 + H_1$ where we know the exact eigenvalues and eigenvectors of H_0 and in some sense H_1 can be considered as "small", i.e. as a perturbation of H_0. A good example is a potential $V(x)$ that has a unique minimum at $x = x_0$. We can then Taylor expand V around x_0, and for x close to this minimum, one can approximate V by the first terms in this Taylor expansions, which is a quadratic (harmonic oscillator) potential, and then $H_0 = \frac{P^2}{2m} + V(x_0) + \frac{1}{2}V''(x_0)(x-x_0)^2$. But as $|x-x_0|$ gets larger, one also has to take into account the higher terms in the Taylor expansion of V, in particular cubic and quartic terms. As long as one can concentrate on the low-lying energy levels (e.g. because the temperature is small) the "particle" will not "explore" much the regions of large x and the deviations from the harmonic potential remain small. It should then make sense to treat these deviations perturbatively.

We will restrict ourselves to the discrete part of the spectrum and normalisable eigenstates. In general, we let

$$H(\lambda) = H_0 + \lambda H_1 \ . \tag{9.1}$$

The parameter λ interpolates between the unperturbed Hamiltonian H_0 and the full (perturbed) Hamiltonian[40] $H_0 + H_1 = H(\lambda = 1)$. We will assume that everything, in particular the eigenvalues and eigenvectors of $H(\lambda)$ depend analytically on λ. More precisely, we assume that they all have a power series expansion in terms of λ which converges[41] (at least) for $|\lambda| \leq 1$. The strategy then is to write the eigenvalue problem for general λ and set $\lambda = 1$ in the end. Hence we have

$$H(\lambda)\,|\varphi_{n,i}(\lambda)\rangle = E_{n,i}(\lambda)\,|\varphi_{n,i}(\lambda)\rangle \ . \tag{9.2}$$

We have split the discrete index into (n, i) as we did when the eigenvalue E_n is degenerate and the extra index i runs over the degeneracies. Here we have also added the index i for the eigenvalues $E_{n,i}$ since we have in mind that typically the non-perturbed energies $E_n(\lambda = 0)$ may be degenerate, but the perturbed energies no longer are : the perturbation has "lifted" the degeneracy. In any case, according to the analyticity assumption we write

$$E_{n,i}(\lambda) = E_n^{(0)} + \lambda E_{n,i}^{(1)} + \lambda^2 E_{n,i}^{(2)} + \dots \ , \tag{9.3}$$

[40] In practice, H_1 often already contains a small parameter, like the parameter η for the harmonic oscillator perturbed by a small uniform electric field, as studied in the last section. One can then use this η as the perturbative parameter and expand all quantities in η. However, we find it more pedagogical to replace η by $\lambda\eta$ and consider η as fixed and vary λ from 0 to 1.

[41] Analyticity and convergence are actually very strong conditions that often are not satisfied. In practice we do not need this much. To do perturbation theory up to some order N, all we need is that we can unambiguously expand our quantities in λ up to order N (with N usually not too large), and that the remainder term can be bounded by some $C_N \lambda^{N+1}$.

and

$$|\varphi_{n,i}(\lambda)\rangle = |\varphi^{(0)}_{n,i}\rangle + \lambda|\varphi^{(0)}_{n,i}\rangle + \lambda^2|\varphi^{(0)}_{n,i}\rangle + \dots \tag{9.4}$$

We then insert these two expansions, as well as $H(\lambda) = H_0 + \lambda H_1$ into (9.2) and equate the terms having the same power of λ. Indeed, the analyticity assumption implies that two power series expansions are equal if and only if the expansion coefficients are equal. We find, at order λ^0, λ and λ^2

$$\begin{aligned} H_0|\varphi^{(0)}_{n,i}\rangle &= E^{(0)}_n|\varphi^{(0)}_{n,i}\rangle \ , \\ H_0|\varphi^{(1)}_{n,i}\rangle + H_1|\varphi^{(0)}_{n,i}\rangle &= E^{(0)}_n|\varphi^{(1)}_{n,i}\rangle + E^{(1)}_{n,i}|\varphi^{(0)}_{n,i}\rangle \ , \\ H_0|\varphi^{(2)}_{n,i}\rangle + H_1|\varphi^{(1)}_{n,i}\rangle &= E^{(0)}_n|\varphi^{(2)}_{n,i}\rangle + E^{(1)}_{n,i}|\varphi^{(1)}_{n,i}\rangle + E^{(2)}_{n,i}|\varphi^{(0)}_{n,i}\rangle \ . \end{aligned} \tag{9.5}$$

The first equation (9.5) is just the unperturbed eigenvector equation, confirming that $E^{(0)}_n$ are the eigenvalues of H_0 and the $|\varphi^{(0)}_{n,i}\rangle$ are the corresponding eigenvectors.

Similarly, writing that the eigenstate $|\varphi_{n,i}(\lambda)\rangle$ as given in (9.4) is normalised to one, $\langle\varphi_{n,i}(\lambda)\,|\varphi_{n,i}(\lambda)\rangle = 1$, and expanding in powers of λ again implies that for each power of λ this equation must be satisfied. This leads to

$$\begin{aligned} \langle\varphi^{(0)}_{n,i}|\varphi^{(0)}_{n,i}\rangle &= 1 \ , \\ \langle\varphi^{(0)}_{n,i}|\varphi^{(1)}_{n,i}\rangle + \langle\varphi^{(1)}_{n,i}|\varphi^{(0)}_{n,i}\rangle &= 0 \ , \\ \langle\varphi^{(0)}_{n,i}|\varphi^{(2)}_{n,i}\rangle + \langle\varphi^{(2)}_{n,i}|\varphi^{(0)}_{n,i}\rangle + \langle\varphi^{(1)}_{n,i}|\varphi^{(1)}_{n,i}\rangle &= 0 \ . \end{aligned} \tag{9.6}$$

But we also know that the phase of $|\varphi_{n,i}(\lambda)\rangle$ is arbitrary and we fix it by requiring that[42]

$$\text{(choice of phase)} \quad \forall\lambda \geq 0 \quad : \quad \langle\varphi^{(0)}_{n,i}\,|\varphi_{n,i}(\lambda)\rangle > 0 \quad \Rightarrow \quad \langle\varphi^{(0)}_{n,i}|\varphi^{(k)}_{n,i}\rangle \geq 0 \ . \tag{9.7}$$

The first equation (9.6) is just the normalisation of the unperturbed eigenstate of H_0. The second equation (9.6) states that the real part of $\langle\varphi^{(0)}_{n,i}|\varphi^{(1)}_{n,i}\rangle$ vanishes. But by the previous choice of phase this means that $\langle\varphi^{(0)}_{n,i}|\varphi^{(1)}_{n,i}\rangle = 0$. Similarly, the third equation (9.6) then relates $\langle\varphi^{(0)}_{n,i}|\varphi^{(2)}_{n,i}\rangle$ to $\langle\varphi^{(1)}_{n,i}|\varphi^{(1)}_{n,i}\rangle$. To summarise,

$$\begin{aligned} \langle\varphi^{(0)}_{n,i}|\varphi^{(1)}_{n,i}\rangle &= 0 \ , \\ \langle\varphi^{(0)}_{n,i}|\varphi^{(2)}_{n,i}\rangle &= -\frac{1}{2}\langle\varphi^{(1)}_{n,i}|\varphi^{(1)}_{n,i}\rangle \ . \end{aligned} \tag{9.8}$$

Let us then exploit the second equation (9.5). If we multiply it with $\langle\varphi^{(0)}_{m,j}|$ and use the fact that this is an eigenvector of H_0 with eigenvalue $E^{(0)}_m$ we get

$$E^{(1)}_{n,i}\langle\varphi^{(0)}_{m,j}|\varphi^{(0)}_{n,i}\rangle = \langle\varphi^{(0)}_{m,j}|H_1|\varphi^{(0)}_{n,i}\rangle + (E^{(0)}_m - E^{(0)}_n)\langle\varphi^{(0)}_{m,j}|\varphi^{(1)}_{n,i}\rangle \ . \tag{9.9}$$

[42] This is not totally obvious. We can always change the overall phase of $|\varphi_{n,i}\rangle\,(\lambda) = |\varphi^{(0)}_{n,i}\rangle + \lambda|\varphi^{(1)}_{n,i}\rangle + \dots$ by multiplying with $e^{i\lambda\alpha+\dots} = 1 + i\lambda\alpha + \dots$ where the $+\dots$ refers to terms of order λ^2 and higher. Then $|\varphi^{(0)}_{n,i}\rangle + \lambda|\varphi^{(1)}_{n,i}\rangle + \dots \to \big(1 + i\lambda\alpha + \dots\big)\big(|\varphi^{(0)}_{n,i}\rangle + \lambda|\varphi^{(1)}_{n,i}\rangle + \dots\big) = |\varphi^{(0)}_{n,i}\rangle + \lambda\big(|\varphi^{(1)}_{n,i}\rangle + i\alpha|\varphi^{(0)}_{n,i}\rangle\big) + \dots$. But this means that $\langle\varphi^{(0)}_{n,i}|\varphi^{(1)}_{n,i}\rangle \to \langle\varphi^{(0)}_{n,i}|\varphi^{(1)}_{n,i}\rangle + i\alpha\langle\varphi^{(0)}_{n,i}|\varphi^{(0)}_{n,i}\rangle = \langle\varphi^{(0)}_{n,i}|\varphi^{(1)}_{n,i}\rangle + i\alpha$. We see that this change of overall phase does not change the real part of $\langle\varphi^{(0)}_{n,i}|\varphi^{(1)}_{n,i}\rangle$ but adds an arbitrary constant to its imaginary part. Obviously, choosing $\alpha = -\,\mathrm{Im}\langle\varphi^{(0)}_{n,i}|\varphi^{(1)}_{n,i}\rangle$ results in a real $\langle\varphi^{(0)}_{n,i}|\varphi^{(1)}_{n,i}\rangle$, as claimed. Redefining the phase by an $e^{i\lambda\alpha+i\lambda^2\beta}$ with appropriate β then also allows to make $\langle\varphi^{(0)}_{n,i}|\varphi^{(2)}_{n,i}\rangle$ real, etc.

If we let $m = n$ this reduces to

$$E^{(1)}_{n,i}\langle\varphi^{(0)}_{n,j}|\varphi^{(0)}_{n,i}\rangle = \langle\varphi^{(0)}_{n,j}|H_1|\varphi^{(0)}_{n,i}\rangle \ . \tag{9.10}$$

- If $E^{(0)}_n$ is non-degenerate, there is no need for the additional index i and we simply get

$$\boxed{E^{(1)}_n = \langle\varphi^{(0)}_n|H_1|\varphi^{(0)}_n\rangle \quad : \quad \text{non-degenerate case} \ ,} \tag{9.11}$$

  i.e. the first-order correction to the energy eigenvalues equals the expectation value of the perturbation H_1 in the unperturbed states $|\varphi^{(0)}_n\rangle$. Next, if we write (9.9) for $m \neq n$ the left-hand side vanishes and this equation can be rewritten as

$$\langle\varphi^{(0)}_{m,j}|\varphi^{(1)}_n\rangle = -\frac{\langle\varphi^{(0)}_{m,j}|H_1|\varphi^{(0)}_n\rangle}{(E^{(0)}_m - E^{(0)}_n)} \quad , \quad (m \neq n) \ . \tag{9.12}$$

  These are the coefficients of the development of $|\varphi^{(1)}_n\rangle$ on the basis of the $|\varphi^{(0)}_{m,j}\rangle$, except for the coefficient $\langle\varphi^{(0)}_n|\varphi^{(1)}_n\rangle$. But we have seen before that this coefficient vanishes. Then the first-order correction to the eigenvector is

$$|\varphi^{(1)}_n\rangle = -\sum_{m\neq n}\sum_j |\varphi^{(0)}_{m,j}\rangle \ \frac{\langle\varphi^{(0)}_{m,j}|H_1|\varphi^{(0)}_n\rangle}{(E^{(0)}_m - E^{(0)}_n)} \ . \tag{9.13}$$

  We may go on and similarly compute the second correction $E^{(2)}_n$ to the eigenvalue and $|\varphi^{(2)}_n\rangle$ to the eigenvector by multiplying the third equation (9.5) by $\langle\varphi^{(0)}_{m,j}|$. Here we will limit ourselves to the correction to the eigenvalue and then it is enough to multiply with $\langle\varphi^{(0)}_n|$. Using then also the first equation (9.8), this yields $E^{(2)}_n = \langle\varphi^{(0)}_n|H_1|\varphi^{(1)}_n\rangle$, which becomes upon using (9.13))

$$\boxed{E^{(2)}_n = \langle\varphi^{(0)}_n|H_1|\varphi^{(1)}_n\rangle = -\sum_{m\neq n}\sum_j \frac{|\langle\varphi^{(0)}_{m,j}|H_1|\varphi^{(0)}_n\rangle|^2}{(E^{(0)}_m - E^{(0)}_n)} \ .} \tag{9.14}$$

- If $E^{(0)}_n$ is degenerate, equation (9.10) reads

$$E^{(1)}_{n,i}\,\delta_{ij} = \langle\varphi^{(0)}_{n,j}|H_1|\varphi^{(0)}_{n,i}\rangle \ , \tag{9.15}$$

  since we can choose the different $|\varphi^{(0)}_{n,i}\rangle$ as orthonormal. A priori, they are any orthonormal basis of the $E^{(0)}_n$ eigenspace. But the above equation actually tells us that the matrix of H_1 in this basis must be diagonal and that the $E^{(1)}_{n,i}$ are the eigenvalues of this matrix. This means that the $|\varphi^{(0)}_{n,i}\rangle$ should be chosen so as to be eigenvectors of $\widehat{H}_1\big|_n$ which is the restriction of H_1

to this $E_n^{(0)}$-eigenspace.[43] Said differently, if one starts with some orthonormal basis in the $E_n^{(0)}$ eigenspace of H_0, one must compute the matrix elements of H_1 in this basis and then the eigenvalues of this matrix provide the (first-order) corrections $E_{n,i}^{(1)}$ to the energies $E_n^{(0)}$. Generically the $E_{n,i}^{(1)}$ are different for different i and one then says that the perturbation has lifted the degeneracy of this level n. One could go on and work out the $|\varphi_{n,i}^{(1)}\rangle$ and the $E_{n,i}^{(2)}$ but we will not do it here.

9.2 The example of the anharmonic oscillator

Let us suppose that we have a particle in a one-dimensional potential $V(x)$ such that $V(x) \to \infty$ as $|x| \to \infty$. Necessarily then V has at least one minimum and we will suppose actually that it has a single minimum at x_0 and no local maxima. This means that $V'(x_0) = 0$ and $V'(x) \neq 0$ for all $x \neq x_0$. We can then always shift the coordinate x by x_0 so that the minimum will be at $x = 0$. We can also adjust the energy by an additive constant[44] so that $V(0) = 0$. Then, Taylor expanding this potential around its minimum we have

$$V(x) = \frac{1}{2}V''(0)x^2 + \frac{1}{6}V'''(0)x^3 + \frac{1}{24}V''''(0)x^4 + \dots \tag{9.16}$$

Of course, we set $V''(0) = m\omega^2$. In section 8 we introduced a characteristic length scale $\gamma = \sqrt{\frac{\hbar}{m\omega}}$, cf (8.4), and then it is useful to rewrite this potential as follows

$$V(x) = \frac{m}{2}\omega^2\big(x^2 + \alpha\frac{x^3}{\gamma} + \beta\frac{x^4}{\gamma^2} + \dots\big)\ , \tag{9.17}$$

with dimensionless constants α and β one can determine in terms of $V'''(0)$ and $V''''(0)$. This way of writing has the advantage to clearly show that the relative importance of the cubic and quartic terms are controlled by the dimensionless quantities $\alpha\frac{x}{\gamma}$ and $\beta\frac{x^2}{\gamma^2}$. In particular, we see that they are small if these dimensionless quantities are small. How small will be clear shortly. We will treat the higher terms in perturbation theory with the unperturbed Hamiltonian H_0 being the Hamiltonian of the harmonic oscillator. Then in the n^{th} eigenstate of H_0 a good measure for x is $\Delta X_n = \sqrt{\frac{\hbar}{2m\omega}(2n+1)} = \gamma\sqrt{n+\frac{1}{2}}$. Then we can estimate $\alpha\frac{x}{\gamma}$ and $\beta\frac{x^2}{\gamma^2}$ to be of the order of $\alpha\sqrt{n+\frac{1}{2}}$ and $\beta\big(n+\frac{1}{2}\big)$. So for small α and β, *and* n not too large, so that $\alpha\sqrt{n+\frac{1}{2}} \ll 1$ and $\beta\big(n+\frac{1}{2}\big) \ll 1$ we expect the corrections due to the cubic and quartic term to be small and the first orders of perturbation theory to give good results.

[43] It may seem surprising that the order λ equation tells us something about the order λ^0 eigenvectors $|\varphi_{n,i}^{(0)}\rangle$ of H_0. Of course, this is not the case. At order λ^0 we may take any basis in the $E_n^{(0)}$-eigenspace. But if we want $|\varphi_{n,i}^{(0)}\rangle + \lambda|\varphi_{n,i}^{(1)}\rangle$ to be the correct eigenvector of $H_0 + \lambda H_1$ also at order λ, then the $|\varphi_{n,i}^{(0)}\rangle$ must be chosen to solve (9.15). If we now take $\lambda \to 0$ we get this particular choice of orthonormal eigenvectors of H_0.

[44] Shifting the potential by a constant V_0 will shift all energy eigenvalues by this same constant V_0 and hence the time-dependence of any state is changed by an overall factor $e^{-iV_0t/\hbar}$. But this overall phase factor affects all states in the same way and drops out from all expectation values or prabability. We conclude that it is irrelevant and we can always shift all energies by the same amount.

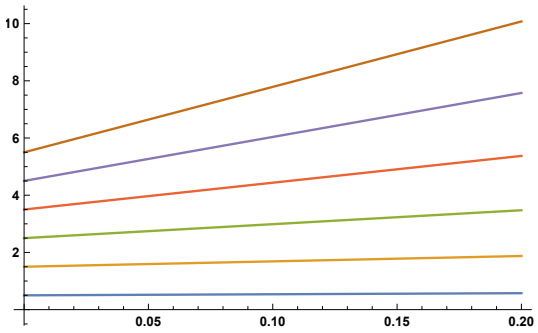
After all these preliminary discussions, it's time to do the computations. We let

$$H = H_0 + H_1 \quad , \quad H_0 = \frac{P^2}{2m} + \frac{m}{2}\omega^2 X^2 \quad , \quad H_1 = \frac{m}{2}\omega^2\big(\frac{\alpha}{\gamma}X^3 + \frac{\beta}{\gamma^2}X^4\big) = \frac{\hbar\omega}{2}\Big(\alpha\frac{X^3}{\gamma^3} + \beta\frac{X^4}{\gamma^4}\Big) \ . \tag{9.18}$$

The eigenvalues and eigenvectors of H_0 are the $E_n^{(0)} = \hbar\omega(n+\frac{1}{2})$ and $|n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle$ as given in section 8. None of the eigenvalues is degenerate, and to first order of perturbation theory we simply have, using that $\langle X^3\rangle_n = 0$ and $\langle X^4\rangle_n = \frac{3}{4}\gamma^4(2n^2+2n+1)$, cf (8.33),

$$E_n^{(1)} = \langle n|\, H_1\, |n\rangle = \frac{\hbar\omega}{2}\,\langle n|\left(\alpha\frac{X^3}{\gamma^3} + \beta\frac{X^4}{\gamma^4}\right)|n\rangle = \frac{3\hbar\omega}{8}\,\beta\,(2n^2+2n+1). \tag{9.19}$$

If we have e.g. $\beta = 10^{-3}$ and $n \leq 10$, the first-order correction $E_n^{(1)}$ is reasonably smaller than the difference $\hbar\omega$ of two adjacent unperturbed energies. The figure shows $(E_n^{(0)} + E_n^{(1)})/(\hbar\omega)$ for the first 6 levels ($n = 0, 1, \ldots 5$) for $0 \leq \beta \leq 0.2$.



The rest of this subsection gives some further illustrations and results for the anharmonic oscillator. Classically, one expects that the x^3 perturbation shifts the minimum of the potential away from $x = 0$. Quantum mechanically this should manifest itself by a non-vanishing expectation value of X. We will establish this result and then use it to give a simple model of thermal dilation. The reader who finds the intermediate computation too "technical" may well skip them without prejudice.

While the cubic term did not contribute to $E_n^{(1)}$ it does contribute to the correction of the eigenvector. Indeed, since $X^3 \sim (a+a^\dagger)^3$ we know that $\langle n\pm 3|\, X^3\, |n\rangle$ and $\langle n\pm 1|\, X^3\, |n\rangle$ are all non-vanishing and contribute in the formula (9.13) for $|\varphi_n^{(1)}\rangle$. As a result, the operator X then gets a non-vanishing expectation value in the new perturbed eigenstate $|n\rangle + |\varphi_n^{(1)}\rangle$. One similarly sees that the quartic terms cannot contribute to the expectation value of X at lowest order.

Exercise 9.1 : *Show that to first order in perturbation theory (which means to order α) we have*

$$\begin{aligned}\langle X\rangle_{n,1} &\equiv \big(\langle n| + \langle\varphi_n^{(1)}|\big)X\big(|n\rangle + |\varphi_n^{(1)}\rangle\big) \\ &= -\alpha\,\langle n|\, X\, |n+1\rangle\,\langle n+1|\,\frac{X^3}{\gamma^3}\,|n\rangle + \alpha\,\langle n|\, X\, |n-1\rangle\,\langle n-1|\,\frac{X^3}{\gamma^3}\,|n\rangle \ .\end{aligned} \tag{9.20}$$

Recall $\frac{X}{\gamma} = \frac{1}{\sqrt{2}}(a + a^\dagger)$ *and* $N = a^\dagger a$ *to show* $\frac{X^3}{\gamma^3} = \frac{1}{2\sqrt{2}}\Big(a^\dagger a^\dagger a^\dagger + 3a^\dagger(N+1) + 3aN + aaa\Big)$ *and conclude*

$$\langle n+1| \frac{X^3}{\gamma^3} |n\rangle = 3\Big(\frac{n+1}{2}\Big)^{3/2} \quad , \quad \langle n-1| \frac{X^3}{\gamma^3} |n\rangle = 3\Big(\frac{n}{2}\Big)^{3/2} \ . \tag{9.21}$$

It is now enough to recall $\langle n| X |n+1\rangle = \frac{\gamma}{\sqrt{2}}\sqrt{n+1}$ and $\langle n| X |n-1\rangle = \frac{\gamma}{\sqrt{2}}\sqrt{n}$ to obtain

$$\langle X\rangle_{n,1} = \Big(\langle n| + \langle\varphi_n^{(1)}|\Big)X\Big(|n\rangle + |\varphi_n^{(1)}\rangle\Big) = 3\alpha\gamma\Big[-\Big(\frac{n+1}{2}\Big)^2 + \Big(\frac{n}{2}\Big)^2\Big] = -\frac{3}{4}\alpha\gamma(2n+1) \ . \tag{9.22}$$

We see that positive α leads to a negative mean-value of X and vice versa.[45]

We can now use this result to make a simple model of thermal dilatation of a crystal. Suppose that at equilibrium the distance ℓ between two neighbouring ions in the crystal is ℓ_0. Then the very small fluctuations around this equilibrium position are harmonic oscillations where X plays the role of $\ell - \ell_0$. In the harmonic approximation, $\langle X\rangle_n = 0$. However, the "true" binding potential will also have cubic and higher terms. We may then interpret our previous result by saying that the cubic term changes the mean distance between two ions to $\ell_0 + \langle X\rangle_{n,1}$ where $\langle X\rangle_{n,1} = -\frac{3}{4}\alpha\gamma(2n+1) = -\frac{3\alpha\gamma}{2\hbar\omega}E_n^{(0)}$. Each bond corrsponds to one such anharmonic oscillator. At zero temperature, all oscillators are in the ground state $n = 0$. But at temperature T one has the Boltzmann probabilities $p(n) = \frac{1}{Z}e^{-E_n/(k_BT)}$ where $Z = \sum_n e^{-E_n/(k_BT)}$, as already discussed in the previous secton. In a first approximation we can take $E_n = E_n^{(0)} = \hbar\omega(n + \frac{1}{2})$. We then compute the thermal average of the $\langle X\rangle_{n,1}$:

$$\langle\langle X\rangle_{n,1}\rangle_T = \sum_{n=0}^{\infty} p_n\langle X\rangle_{n,1} = \frac{1}{Z}\sum_{n=0}^{\infty} e^{-E_n^{(0)}/(k_BT)}\big(-\frac{3\alpha\gamma}{2\hbar\omega}\big)E_n^{(0)} = -\frac{3\alpha\gamma}{2\hbar\omega}\ \frac{U}{N} \simeq -\frac{3\alpha\gamma}{2\hbar\omega}\ k_BT \ , \tag{9.23}$$

where the last $\simeq$ holds for temperatures $k_BT \gg \hbar\omega$, as seen in the previous section. We interpret this now by saying that the mean distance between the ions in the crystal increases / decreases linearly with the temperature if $\alpha < 0$ / $\alpha > 0$. Thus the thermal dilatation coefficient $\frac{1}{\ell}\frac{\partial\ell}{\partial T}$ equals $-\frac{3\alpha\gamma k_B}{2\hbar\omega\ell_0}$.

One could go on and determine $E_n^{(2)}$ as

$$E_n^{(2)} = -\sum_{n'\neq n} \frac{|\langle n'| H_1 |n\rangle|^2}{\hbar\omega(n'-n)} = -\sum_{n'\neq n} \frac{\Big|\langle n'|\Big(\alpha\frac{X^3}{\gamma^3} + \beta\frac{X^4}{\gamma^4}\Big)|n\rangle\Big|^2}{2(n'-n)} \tag{9.24}$$

Now both terms $\sim \alpha X^3$ and βX^4 contribute and the sum contains all terms with n' ranging from $n-4$ to $n+4$. The explicit computation is a bit lengthy and we will leave it as an exercise :

Exercise 9.2 : *In addition to* (9.21)*, also determine* $\langle n \pm 3| \frac{X^3}{\gamma^3} |n\rangle$ *along the same lines. Compute similarly* $\frac{X^4}{\gamma^4}$ *writing it as much as possible in terms of* N *and then determine the* $\langle n'| \frac{X^4}{\gamma^4} |n\rangle$ *which are non-vanishing only for* $n' = n, n \pm 2, n \pm 4$*. Using these results, compute* $E_n^{(2)}$ *according to* (9.24)*.*

[45] This is in agreement with the fact that adding an x^3-term with a positive coefficient to the harmonic potential lowers the potential for the negative x-values, making it classically "more accessible".

9.3 Time dependent perturbations

We will now study what happens if the perturbation H_1 is time-dependent, so it is actually a $H_1(t)$. There can be many situations, in particular we can consider the case where a constant perturbation is "turned on" at some time t_0 and then again turned off at time $t_0 + T$, so that it only acts over some time interval T. Similarly we can have an oscillating perturbation that we turn on and off after some T. We may consider the limits of small or large T. The interaction of an atom with light corresponds to such a perturbation by an oscillating electric field.

Contrary to the stationary perturbation theory where one determines the eigenvalues and eigenvectors of the perturbed Hamiltonian $H_0 + H_1$, in time-dependent perturbation theory one typically starts with an eigenstate of H_0 at some initial time t_i and asks what is the probability, due to the perturbation H_1, that the system is in another eigenstate of H_0 at some final time $t_f = t_i + T$.

Quite generally, we let again

$$H = H_0 + H_1(t) \quad , \quad H_0|\varphi^{(0}_{n,i}\rangle = E^{(0)}_n|\varphi^{(0}_{n,i}\rangle \ . \tag{9.25}$$

A general state $|\psi(t)\rangle$ can always be developed on the basis of the $|\varphi^{(0}_{n,i}\rangle$. We know that in the absence of H_1 the coefficients would have a time dependence $\sim e^{-iE^{(0)}_n(t-t_0)/\hbar}$ so we write

$$|\psi(t)\rangle = \sum_{n,i} c_{n,i}(t) e^{-iE^{(0)}_n(t-t_0)/\hbar}|\varphi^{(0}_{n,i}\rangle \ , \tag{9.26}$$

To simplify the notations in the sequel, we suppress the index i with the understanding that either there is no degeneracy, or that the label n now also includes the degeneracy index (so that E_n and E_m do not necessarily denote different energies even if $n \neq m$). The Schrödinger equation results in

$$\sum_n i\hbar\, \dot{c}_n(t) e^{-iE^{(0)}_n(t-t_0)/\hbar}|\varphi^{(0}_n\rangle = \sum_n c_n(t) e^{-iE^{(0)}_n(t-t_0)/\hbar} H_1(t)|\varphi^{(0}_n\rangle \ , \tag{9.27}$$

and multiplying by $\langle\varphi^{(0)}_m|$ gives

$$i\hbar\, \dot{c}_m(t) = \sum_n e^{-i(E^{(0)}_n - E^{(0)}_m)(t-t_0)/\hbar} \langle\varphi^{(0)}_m|H_1(t)|\varphi^{(0}_n\rangle\, c_n(t) \ . \tag{9.28}$$

We will now solve this (infinite) system of first-order differential equations with time dependent coefficients, by proceeding again perturbatively. We consider that H_1 actually is λH_1 and develop

$$c_n(t) = c^{(0)}_n(t) + \lambda\, c^{(1)}_n(t) + \lambda^2 c^{(2)}_n(t) + \dots \tag{9.29}$$

Then, identifying the different powers of λ leads to

$$\begin{aligned}
i\hbar\, \dot{c}^{(0)}_m(t) &= 0 \ , \\
i\hbar\, \dot{c}^{(1)}_m(t) &= \sum_n e^{-i(E^{(0)}_n - E^{(0)}_m)(t-t_0)/\hbar} \langle\varphi^{(0)}_m|H_1(t)|\varphi^{(0}_n\rangle\, c^{(0)}_n(t) \ , \\
i\hbar\, \dot{c}^{(2)}_m(t) &= \sum_n e^{-i(E^{(0)}_n - E^{(0)}_m)(t-t_0)/\hbar} \langle\varphi^{(0)}_m|H_1(t)|\varphi^{(0}_n\rangle\, c^{(1)}_n(t) \ ,
\end{aligned} \tag{9.30}$$

etc. The first equation just states that the $c_n^{(0)}$ are constant and equal to their initial values. Inserting this into the second equation completely determines its right-hand side and upon integrating one obtains $c_n^{(1)}(t)$. One can then proceed similarly with the third equation to obtain $c_n^{(2)}(t)$, etc. Here we will satisfy ourselves with this first-order approximation, i.e. $c_n^{(1)}(t)$.

We will assume that initially, at some time t_0, the system is in an eigenstate of H_0 (this makes sense in particular if $H_1(t) = 0$ for $t \leq t_0$), and that a single coefficient $c_{n_i}^{(0)}(t_0) = 1$ is non-vanishing, while all $c_n^{(r)}(t_0)$ vanish for $r \geq 1$. Since the $c_n^{(0)}$ are constant, we have for all t that $c_n^{(0)}(t) = \delta_{nn_i}$. Then the second equation (9.30) becomes

$$i\hbar\, \dot{c}_m^{(1)}(t) = e^{-i(E_{n_i}^{(0)} - E_m^{(0)})(t-t_0)/\hbar} \langle \varphi_m^{(0)} | H_1(t) | \varphi_{n_i}^{(0} \rangle \ , \tag{9.31}$$

which is integrated as

$$c_m^{(1)}(t) = \frac{1}{i\hbar} \int_{t_0}^{t} \mathrm{d}t'\, e^{-i(E_{n_i}^{(0)} - E_m^{(0)})(t'-t_0)/\hbar} \langle \varphi_m^{(0)} | H_1(t') | \varphi_{n_i}^{(0} \rangle \ . \tag{9.32}$$

To go further, we need to make some assumption about the time dependence of $H_1(t)$ or actually of the matrix elements $\langle \varphi_m^{(0)} | H_1(t) | \varphi_{n_i}^{(0} \rangle$.

Constant perturbation for a finite time interval : Suppose that one switches on a constant perturbation H_1 at the initial time t_0 and then switches it off again after some interval T, i.e. at $t = t_0 + T$. Then the time integral is trivial. If we assume that $m \neq n_i$ and $E_m^{(0)} - E_{n_i}^{(0)} \equiv \hbar\omega_{m,n_i} \neq 0$ then for all $t \geq t_0 + T$ one has

$$\begin{aligned} c_m^{(1)}(t) &= \frac{1}{i\hbar} \langle \varphi_m^{(0)} | H_1 | \varphi_{n_i}^{(0} \rangle \int_{t_0}^{t_0+T} \mathrm{d}t'\, e^{i\omega_{m,n_i}(t'-t_0)} = -\frac{1}{\hbar} \langle \varphi_m^{(0)} | H_1 | \varphi_{n_i}^{(0} \rangle \frac{e^{i\omega_{m,n_i}T} - 1}{\omega_{m,n_i}} \\ &= -\frac{i}{\hbar} e^{i\omega_{m,n_i}T/2} \langle \varphi_m^{(0)} | H_1 | \varphi_{n_i}^{(0} \rangle \ \frac{\sin\left(\omega_{m,n_i}T/2\right)}{\omega_{m,n_i}/2} \end{aligned} \tag{9.33}$$

The transition probability from an initial state $|\varphi_{n_i}^{(0)}\rangle$ to a final state $|\varphi_{n_f}^{(0)}\rangle$ (we write n_f instead of m and $\hbar\omega_{n_f,n_i} = E_{n_f} - E_{n_i}$) then is

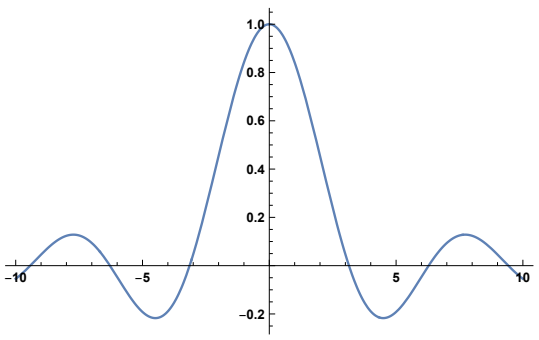
$$P(n_i \to n_f, t \geq t_0 + T) = \frac{T^2}{\hbar^2} |\langle \varphi_{n_f}^{(0)} | H_1 | \varphi_{n_i}^{(0)} \rangle|^2 \ \left(f(\omega_{n_f,n_i}T/2)\right)^2, \tag{9.34}$$

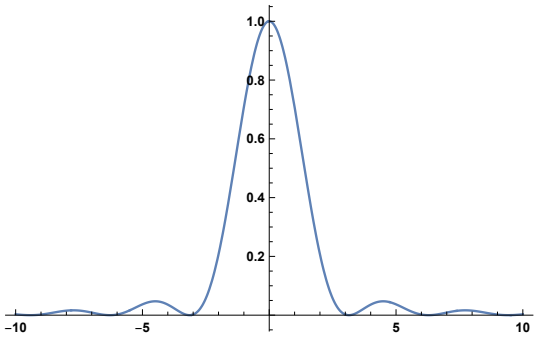
where we defined

$$f(x) = \frac{\sin x}{x} \ . \tag{9.35}$$

We derived the previous transition probability for the case $E_{n_f} \neq E_{n_i}$. If instead, the initial energy level was degenerate and the final state corresponds to the same energy, the time integral simply gives a factor T and one gets for the probability $\frac{T^2}{\hbar^2} |\langle \varphi_{n_f}^{(0)} | H_1 | \varphi_{n_i}^{(0} \rangle|^2$. But this is also obtained from (9.34) for $\omega_{n_f,n_i} = 0$ since $f(0) = 1$, so this formula is valid whether we deal with degenerate levels or not.

The function $f(x) = \frac{\sin x}{x}$ and its square $f^2(x) = \frac{\sin^2 x}{x^2}$ are shown in the figure below. They both have a peak at $x = 0$ and a width of about $\Delta x = \pi$. Of course, the peak is more pronounced





for f^2. We see that the transition probability (9.34) is non-negligible for large T only if ω_{n_f,n_i} is small. In any case, for our perturbative scheme to remain valid, the coefficients $c_{n_f}^{(1)}$ and the transition probabilities must remain small.

Oscillating perturbation for a finite time interval : Suppose now that one still switches on the perturbation $H_1(t)$ at $t = t_0$ and then off at $t = t_0 + T$, but now with an oscillating $H_1(t) = \widehat{H}_1\big(e^{i\omega(t-t_0)} + e^{-i\omega(t-t_0)}\big)$. Then the integral (9.32) gives for $t \geq t_0 + T$:

$$\begin{aligned} c_{n_f}^{(1)}(t) &= \frac{1}{i\hbar}\,\langle\varphi_{n_f}^{(0)}|\widehat{H}_1|\varphi_{n_i}^{(0}\rangle \int_{t_0}^{t_0+T} \mathrm{d}t'\, e^{i\omega_{n_f,n_i}(t'-t_0)}\big(e^{i\omega(t-t_0)} + e^{-i\omega(t-t_0)}\big) \\ &= -\frac{1}{\hbar}\,\langle\varphi_{n_f}^{(0)}|\widehat{H}_1|\varphi_{n_i}^{(0}\rangle \left[\frac{e^{i(\omega_{n_f,n_i}+\omega)T}-1}{\omega_{n_f,n_i}+\omega} + \frac{e^{i(\omega_{n_f,n_i}-\omega)T}-1}{\omega_{n_f,n_i}-\omega}\right] \\ &= -i\frac{T}{\hbar}\,\langle\varphi_{n_f}^{(0)}|\widehat{H}_1|\varphi_{n_i}^{(0}\rangle \left[e^{i(\omega_{n_f,n_i}+\omega)\frac{T}{2}} f\Big(\frac{(\omega_{n_f,n_i}+\omega)T}{2}\Big) + e^{i(\omega_{n_f,n_i}-\omega)\frac{T}{2}} f\Big(\frac{(\omega_{n_f,n_i}-\omega)T}{2}\Big)\right] \end{aligned} \tag{9.36}$$

The frequency ω is taken as positive, while the ω_{n_f,n_i} can be either positive or negative. Although less than f^2, the function f still is considerably peaked and from the two terms present, the one with the smaller argument will dominate. If $\omega_{n_f,n_i} > 0$ this is the second term, and if $\omega_{n_f,n_i} < 0$ this is the first one. In any case, the dominant term contains a $f\big((\omega - |\omega_{n_f,n_i}|)T/2\big)$ (since f is an even function). Hence

$$P(n_i \to n_f, t \geq t_0 + T) \simeq \frac{T^2}{\hbar^2}|\langle\varphi_{n_f}^{(0)}|\widehat{H}_1|\varphi_{n_i}^{(0}\rangle|^2 \left(f\Big(\frac{(\omega - |\omega_{n_f,n_i}|)T}{2}\Big)\right)^2 . \tag{9.37}$$

If we switch on this periodic perturbation for a large time T, then the transition probability will have a sharp maximum for those transitions that have an ω_{n_f,n_i} very close to either ω or $-\omega$. (The first case corresponds to the processes of absorption and the second case to stimulated emission.) On the other hand, if T is small, the transition probabilities for $n_i \to n_f$ will not vary much over an interval of about $\Delta\omega_{n_f,n_i} \sim \frac{\pi}{T}$ around ω. This is sometimes stated as a sort of uncertainty relation between energy and time (writing ΔT instead of T) :

$$\Delta E \Delta T \simeq \pi\hbar\ . \tag{9.38}$$

However, one should keep in mind that this is very different from $\Delta X \Delta P \geq \frac{\hbar}{2}$ where ΔX and ΔP have a precise meaning and the inequality is strictly proven.

It is also worth noting that for $\omega = |\omega_{n_f,n_i}|$, where the transition probability takes its maximal value, it grows with time as T^2, namely as $(\Omega T)^2$ where $\hbar\Omega = |\langle\varphi^{(0)}_{n_f}|H_1|\varphi^{(0}_{n_i}\rangle|$. This T^2-growth is valid for discret energy values ω_{n_f,n_i} and, of course, as long as the transition probability remains small so that our perturbation theory is valid. It is perfectly compatible with the exact results we have obtained for the transition probabilities studied in sections 3 and 4 which typically behaved as $P(i \to f, T) \sim \sin^2 \Omega T \sim (\Omega T)^2$ as long as $T\Omega \ll 1$, i.e. as long as the transition probability remains small. On the other hand, for ω_{n_f,n_i} in the continuous spectrum, the transition probability to a given energy interval grows as T, as we will discuss in the next subsection.

Exercise 9.3 : *Consider a charged particle in a harmonic oscillator potential in the presence of an "electromagnetic wave" corresponding to a* $H_1 = h_1 + h_1^\dagger$ *with* $h_1 = \epsilon e^{i\omega(t-t_0)-ikX}$. *With* $n_i = 0$ *and* n_f *a positive integer one must compute* $\langle n_f|\, e^{-ikX}\,|0\rangle = \langle n_f|\, e^{-ik\gamma(a+a^\dagger)/\sqrt{2}}\,|0\rangle$. *Using Glauber's formula, rewrite this as* $c\,\langle n_f|\, e^{-ik\gamma a^\dagger/\sqrt{2}} e^{-ik\gamma a/\sqrt{2}}\,|0\rangle$ *with a constant* c *to be determined, and conclude that*

$$\langle n_f|\, H_1\,|0\rangle = \frac{c}{\sqrt{n_f!}}\big(-ik\gamma/\sqrt{2}\big)^{n_f} e^{i\omega(t-t_0)} + c.c. \tag{9.39}$$

9.4 Fermi's golden rule

We already noted that the function $f(x)$, and even more $f^2(x)$, is strongly peaked around $x = 0$, and this implied that the transition probability was non-negligible only for certain energy differences, either $\omega_{f,i} \simeq 0$ for the constant perturbation, or $\omega_{f,i} \simeq \pm\omega$ for an oscillating perturbation with frequency ω. We also saw that the transition probability grows with the time T for which the perturbation is switched on. We had pulled out an explicit factor T^2 in order to have the function f^2 appear, but as we will show now, for a continuum of accessible states, the growth is actually proportional to T, so that it makes sense to define a transition *rate* as the transition probability after a (large) time T, divided by T :

$$\Gamma(n_i \to n_f) \sim_{T\to\infty} \frac{1}{T}\, P(n_i \to n_f, t \geq t_0 + T)\ , \tag{9.40}$$

where it is implicitly understood that we consider switching on a very small perturbation for a very long time T. Indeed, for our perturbation theory to make sense, the total transition probability must remain small, and since it grows with time, the matrix elements $|\langle\varphi^{(0)}_{n_f}|H_1|\varphi^{(0)}_{n_i}\rangle|^2$ must be small enough.

We can treat both cases of constant and oscillating perturbation simultaneously, since (9.34) is recovered from (9.37) by simply setting $\omega = 0$. (The absolute value of $\omega_{f,i}$ then is irrelevant since f is an even function of its argument.) Thus

$$\Gamma(n_i \to n_f) \sim_{T\to\infty} \frac{1}{\hbar^2}|\langle\varphi^{(0)}_{n_f}|\widehat{H}_1|\varphi^{(0)}_{n_i}\rangle|^2\ T\, f^2\Big(\frac{(\omega - |\omega_{n_f,n_i}|)T}{2}\Big)\ . \tag{9.41}$$

Let us study a bit more closely this large T limit. We let

$$g_T(x) = \frac{T}{2\pi}\, f^2(x\,T/2) = \frac{2}{\pi\,T}\frac{\sin^2(x\,T/2)}{x^2}\ . \tag{9.42}$$

One has $\int_{-\infty}^{\infty} \mathrm{d}z \frac{\sin^2 z}{z^2} = \pi$ as one can easily show by the residue theorem.[46] Then, by a simple change of variables, one also sees that

$$\int_{-\infty}^{\infty} \mathrm{d}x \, g_T(x) = 1 \ , \tag{9.43}$$

independently of the value of T. But we have seen that for very large T, $f^2(xT/2)$ is narrowly peaked around $x = 0$. Thus, in the limit of very large T, the function $g_T(x)$ behaves exactly as a Dirac delta and we write

$$g_T(x) \sim_{T\to\infty} \delta(x) \ , \tag{9.44}$$

so that finally

$$\Gamma(n_i \to n_f) = \frac{2\pi}{\hbar^2} |\langle \varphi^{(0)}_{n_f} | \widehat{H}_1 | \varphi^{(0)}_{n_i} \rangle|^2 \ \delta(|\omega_{f,i}| - \omega) \ , \tag{9.45}$$

or in terms of the energies (recall $\delta(ax) = \frac{1}{|a|}\delta(x)$)

$$\Gamma(n_i \to n_f) = \frac{2\pi}{\hbar} |\langle \varphi^{(0)}_{n_f} | \widehat{H}_1 | \varphi^{(0)}_{n_i} \rangle|^2 \ \delta(|E_{f,i}| - E) \ . \tag{9.46}$$

Of course, to make sense of the Dirac delta, it should be integrated over some energy or frequency interval. Let us then assume that there is a continuum of final states with varying energies E_f, and that the matrix elements depend smoothly on E_f. We should then sum (integrate) the transition rate over all allowed final states which amounts to suppressing the Dirac delta in the previous formula. More generally there can be many final states with the corresponding final energy. Formally, we integrate over all final states $\int \mathrm{d}N_f$. This integration "includes" an integration over the final energies E_f and the Dirac delta picks out those states that have the correct final energy. The density $\rho(E_F)$ of final states per unit interval of energy (not to be confused with the density operator) is defined such that[47] $\int \mathrm{d}N_f = \int \mathrm{d}E_f \, \rho(E_f)$. Then with

$$\Gamma(i \to f) = \int \mathrm{d}N_f \, \Gamma(n_i \to n_f) = \int \mathrm{d}E_f \, \rho(E_f) \, \Gamma(n_i \to n_f) \ , \tag{9.47}$$

we finally get

$$\boxed{\Gamma(i \to f) = \frac{2\pi}{\hbar} |\langle \varphi^{(0)}_{n_f} | \widehat{H}_1 | \varphi^{(0)}_{n_i} \rangle|^2 \, \rho(E_f) \quad , \quad |E_f - E_i| = \hbar\omega \ .} \tag{9.48}$$

This is Fermi's golden rule.

[46] First note that the integrand is regular at $z = 0$. One can slightly deform the integration contour away from the real axis to lie just below it in the complex plane, i.e. to go from $-\infty - i\epsilon$ to $\infty - i\epsilon$., Then one can decompose $\sin^2 z = \frac{1}{4}(2 - e^{2iz} - e^{-2iz})$. For the first and third term on can close the integration contour by a large semi-circle in the lower complex plane. Then this contour does not enclose the pole at $z = 0$ and the integral vanishes. For the second term e^{iz}, however, we must close the contour by a large semi-circle in the upper half plane, and then it encloses the double pole at $z = 0$, so that the integral equals $2\pi i \frac{1}{4}(-)\frac{\mathrm{d}e^{2iz}}{\mathrm{d}z}\big|_{z=0} = \pi$.

[47] As an example, consider a radioactive decay, where the final energy could be simply the kinetic energy of a decay particle, and the different final states correspond to all possible final momenta $\vec{p}_f$ of this particle. With periodic boundary conditions in a large box of size L, we have $\vec{p}_f = \frac{2\pi}{L}\vec{n}_f$ so that $\mathrm{d}N_f = \left(\frac{L}{2\pi\hbar}\right)^3 \mathrm{d}^3 p_f = \left(\frac{L}{2\pi\hbar}\right)^3 \mathrm{d}^2\Omega \, p_f^2 \mathrm{d}p_f$. On the other hand, $E_f = \frac{p_f^2}{2m}$ so that $\mathrm{d}E_f = \frac{p_f}{m}\mathrm{d}p_f$ and then $\mathrm{d}^3 p_f = \mathrm{d}^2\Omega \, m^{3/2}(2E_f)^{1/2}\mathrm{d}E_f$. Integrating over the angles gives a 4π, so that the density of states is $\rho(E_f) = \left(\frac{L}{2\pi\hbar}\right)^3 4\pi m^{3/2}(2E_f)^{1/2}$.