Master QLMN
Revision week

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Approximation methods in Quantum Physics

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Exact solutions to most problems in quantum physics, as in all other fields of physics, do not exist despite the fact that the equations to solve are known. Numerical calculations are often possible (but not always...) using computers. Approximate methods are therefore fruitful to get quick estimates, check the plausibility of a numerical result, and to gain intuition on physical effects. Here we summarize and illustrate widely used approximation methods: time-independent perturbation theory, including the variational method and the effective hamiltonian approach; time-dependent perturbation theory and "Fermi golden rule". We will follow a practical approach, avoiding the usual lengthy derivations and justifications. More details can be found in standard textbooks, such as: "Mécanique quantique" by J.-L. Basdevant and J. Dalibard, chapters 9 and 17, or on Wikipedia.

Most situations in perturbation theory start from a problem that we know how to solve. There are not that many of them: particle in an infinite square well or harmonic potential, charged particle in a Coulomb potential, spin in a magnetic field, and that is about it. In practice this means having solved the eigenvalue problem: $H_0 |\phi_n\rangle = E_n |\phi_n\rangle$, with H_0 the hamiltonian describing the problem. One then adds a perturbation $\hat{V}$ (which may be time-dependent), assumed to be small in a sense which usually means that the matrix elements $V_{kn} = \langle\phi_k| \hat{V} |\phi_n\rangle \ll |E_k - E_n|$.

1 Time-independent perturbation theory

Here, the goal is to calculate the corrections to the eigen-energies and eigen-states as a function of a small parameter $\epsilon \sim V_{kn}/|E_k - E_n|$. We will not discuss the problem of the convergence of the expansion in ϵ. Most general results can be easily inferred from the study of the two-level system, which we thus start with.

1.1 The two-level system

We consider two states $|g\rangle$ and $|e\rangle$ associated to the energies E_g and E_e supposed to be known. The perturbation $\hat{V}$ has matrix elements $V_{gg} = \langle g| \hat{V} |g\rangle$, $V_{ee} = \langle e| \hat{V} |e\rangle$, $V_{ge} = \langle g| \hat{V} |e\rangle = V_{eg}$ and the total hamiltonian is:

$$H = H_0 + \hat{V} = \begin{pmatrix} E_g & 0 \\ 0 & E_e \end{pmatrix} + \begin{pmatrix} V_{gg} & V_{ge} \\ V_{eg} & V_{ee} \end{pmatrix} \ . \tag{1}$$

A convenient procedure to quickly diagonalize the 2×2 matrix consists in writing it in the following form:

$$H = \frac{1}{2}(E_g + E_e + V_{gg} + V_{ee})\,\hat{\mathbf{Id}} + \frac{1}{2}\sqrt{\Delta E^2 + 4V_{eg}^2}\begin{pmatrix} -\cos\theta & \sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \tag{2}$$

with $\Delta E = E_e + V_{ee} - E_g - V_{gg}$, $\cos\theta = \Delta E/\sqrt{\Delta E^2 + 4V_{eg}^2}$, $\sin\theta = 2V_{eg}/\sqrt{\Delta E^2 + 4V_{eg}^2}$. The eigen-energies and corresponding eigenstates are:

$$E_- = \frac{1}{2}(E_g + E_e + V_{gg} + V_{ee}) - \frac{1}{2}\sqrt{\Delta E^2 + 4V_{eg}^2} \quad\text{and}\quad |\tilde{g}\rangle = \cos\frac{\theta}{2}\,|g\rangle - \sin\frac{\theta}{2}\,|e\rangle \tag{3}$$

$$E_+ = \frac{1}{2}(E_g + E_e + V_{gg} + V_{ee}) + \frac{1}{2}\sqrt{\Delta E^2 + 4V_{eg}^2} \quad\text{and}\quad |\tilde{e}\rangle = \cos\frac{\theta}{2}\,|e\rangle + \sin\frac{\theta}{2}\,|g\rangle\,. \tag{4}$$

So far the results are exact. Let us now Taylor expand the expressions of the energies and states as a function of $\epsilon \sim V_{nm}/|E_e - E_g|$, using $\sqrt{1+x} \approx 1 + x/2 + O(x^2)$:

$$E_- \approx E_g + V_{gg} - \frac{V_{eg}^2}{E_e - E_g} + \ldots \quad\text{and}\quad |\tilde{g}\rangle \approx |g\rangle - \frac{V_{eg}}{E_e - E_g}\,|e\rangle + \ldots \tag{5}$$

$$E_+ \approx E_e + V_{ee} + \frac{V_{eg}^2}{E_e - E_g} + \ldots \quad\text{and}\quad |\tilde{e}\rangle \approx |e\rangle + \frac{V_{eg}}{E_e - E_g}\,|g\rangle + \ldots \tag{6}$$

Here the energies are expanded up to second order in ϵ and the state to first order. These expressions call for three important remarks (see also Fig. 1a).

1. The first-order corrections on the energy $E_{g,e}$ are the average values of the perturbation $\hat{V}$ for the *unperturbed* states.

2. The second-order correction always pushes the coupled states away: they "repel" each other.

3. The effect of the coupling is to admix the unperturbed states to other states. For example, one says that the $|g\rangle$ state "acquires some excited state character". This is jargon, but worth remembering...It has important applications: giving a lifetime to a ground state by admixing it with an excited state, enhancing the strength of interactions between atoms by coupling their ground state to states where they strongly interact,...

1.2 General case

All quantum physics textbooks derive the corrections to the energies and states as a power expansion of the perturbation written in the form $\epsilon\hat{V}$, with $\epsilon \ll 1$. However the final results can be inferred from the two-level case of the previous section: if a given unperturbed state $|\phi_n\rangle$ of an hamiltonian H_0 is coupled to other states $|\phi_k\rangle$ (including itself...) by a perturbation $\hat{V}$, one adds independently the effect of all two-level systems (n, k) (see Fig. 1b), leading to the second order expression for the energies:

$$\tilde{E}_n = E_n + \langle\phi_n|\,\hat{V}\,|\phi_n\rangle + \sum_{k\neq n}\frac{\langle\phi_n|\,\hat{V}\,|\phi_k\rangle\,\langle\phi_k|\,\hat{V}\,|\phi_n\rangle}{E_n - E_k} + \ldots, \tag{7}$$

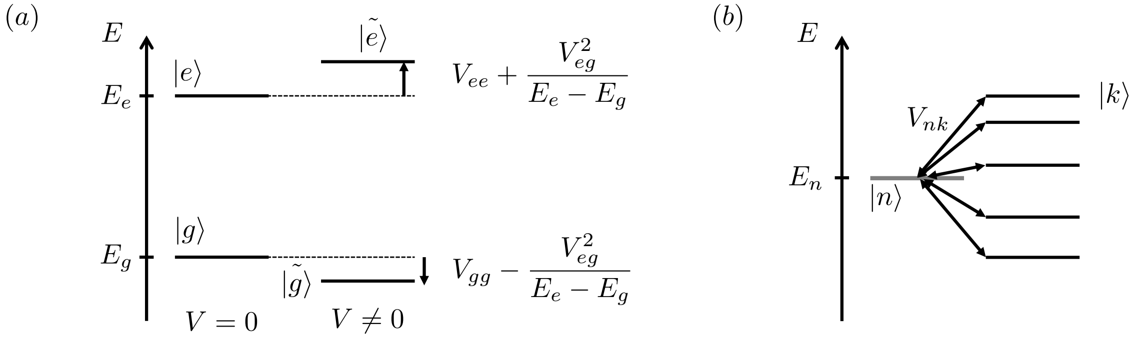

Figure 1: *Time independent perturbation theory. (a) Case of a two-level system. (b) General case.*

with $\langle\phi_n| \hat{V} |\phi_k\rangle \langle\phi_k| \hat{V} |\phi_n\rangle = |V_{nk}|^2$, and the first-order expression for the states.

$$|\tilde{\phi_n}\rangle = |\phi_n\rangle + \sum_{k \neq n} |\phi_k\rangle \frac{\langle\phi_k| \hat{V} |\phi_n\rangle}{E_n - E_k} + ... \tag{8}$$

The second-order expression for the states is rarely used. These expressions are worth remembering. To recall the sign of the denominator $E_n - E_k$, remember that the perturbation always shifts down the energy of the ground state and that $E_{\text{gs}} - E_k < 0$.

Degenerate case. The above expressions have an obvious flaw when the energies E_n are degenerate, i.e., $g_n > 1$ orthogonal states $|\phi_n^\alpha\rangle$ $(1 \leq \alpha \leq g_n)$ have the same energy: the denominator of the expression (7) is 0 for some states, and the perturbative approach is not valid. In this case, the zeroth-order eigenstates and the first-order energies are obtained by diagonalizing $H_0 + \hat{V}$ in each subspace $\mathcal{E}_n$ associated to the energy E_n.

1.3 Examples (solutions in Appendix)

A. Zeeman effect on an atom. The atomic states are characterized by several quantum numbers: n, j and m_j, the two last ones being associated to the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$. The atom possesses a magnetic moment $\boldsymbol{\mu} = \gamma \mathbf{J}$. Calculate the energies of the atom placed in a magnetic field B aligned along the z-axis.

B. Non-harmonic oscillator. Consider an oscillator with $H = p^2/(2m) + m\omega^2 x^2/2 + gx^4$. Remembering that $x = x_0(a + a^+)$, with $x_0 = \sqrt{\hbar/(2m\omega)}$, calculate the energy shift of the ground state $|n = 0\rangle$.

C. Stark shift of an atom and polarizability. Place an hydrogen atom in an electric field E. The hamiltonian is $H_\text{S} = q\hat{z}E$. Calculate the energy shift of the ground state, and the expression of the polarizability α, defined by $\Delta E_{\text{gs}} = -\epsilon_0 \alpha E^2/2$. Calculate the perturbed ground state, and explain why the atom now has an average dipole moment.

D. Van der Waals interaction between two atoms. Two neutral atoms interact by the dipole-dipole interaction described by the hamiltonian: $H_\text{I} = \hat{d}_{1z}\hat{d}_{2z}/(4\pi\epsilon_0 R^3)$

(we neglect here the angular dependence). Assume that each atom has two states, for example ψ_{ns} and ψ_{np} as in alkali atoms, separated by an energy $\hbar\omega_0$. Explain why the ground-state interaction energy is of the form $-C_6/R^6$ and calculate C_6.

E. Light-shift induced by a laser. A two-level atom with states $|g\rangle$ and $|e\rangle$, separated by a transition at frequency ω_0 is coupled to a laser field (frequency ω), containing N photons. We consider the (atom + field) system with states $|g, N\rangle$ and $|e, N-1\rangle$, and a matrix element $\hbar\Omega$ coupling the two. Calculate the energy shift of the states as a function of Ω and the detuning $\Delta = \omega - \omega_0$ for $\Omega \ll |\Delta|$.

2 The effective hamiltonian approach

In many situations, the spectrum of the unperturbed hamiltonian consists of manifolds were states are close in energy, the various manifolds being separated by a large energy gap, as represented in Fig. 2(a). This situation is often encountered in condensed matter with energy bands or in atoms with hyperfine and optical transitions. We assume that the perturbation $\hat{V}$ only has matrix elements between states belonging to *different* manifolds. We will see that, as a consequence of the perturbation, states within a manifold get coupled, and that the situation can be described by an effective hamiltonian.

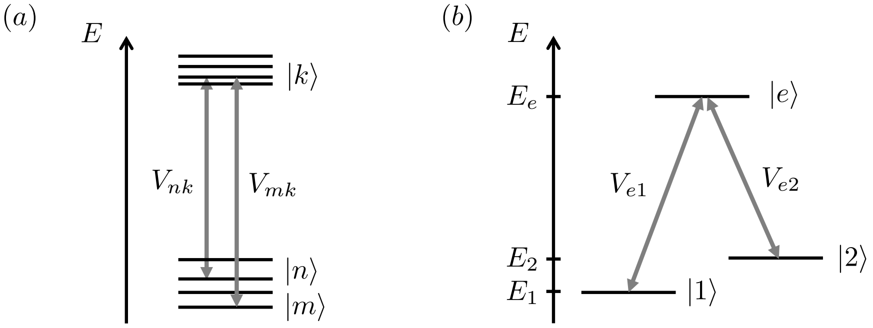

Figure 2: *Effective hamiltonian. (a) The spectrum consists of several manifolds of states with comparable energies, separated by a gap. (b) Three-state model.*

2.1 A three-state model

Consider the simplest situation or two states $|1\rangle$ and $|2\rangle$, with energies $E_{1,2}$, and a third state $|e\rangle$ with energy E_e such that $|E_e - E_{1,2}| \gg |E_1 - E_2|$, as shown in Fig. 2(b). The perturbation couples $|1\rangle$ and $|2\rangle$ to $|e\rangle$ with matrix element V_{1e} and V_{2e}. The matrix of the hamiltonian is:

$$H = \begin{pmatrix} E_1 & 0 & V_{1e} \\ 0 & E_2 & V_{2e} \\ V_{e1} & V_{e2} & E_e \end{pmatrix} . \qquad (9)$$

Any state of the system has the form $|\psi\rangle = c_1 |1\rangle + c_2 |2\rangle + c_3 |3\rangle$. Finding the eigenenergies amounts to solving the system of coupled equations:

$$\begin{pmatrix} E_1 & 0 & V_{1e} \\ 0 & E_2 & V_{2e} \\ V_{e1} & V_{e2} & E_e \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_e \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_e \end{pmatrix} . \tag{10}$$

Here $c_{1,2}$ depend on c_e. Using the third equation

$$c_e = \frac{1}{E - E_e}(V_{e1}c_1 + V_{e2}c_2) \tag{11}$$

and eliminating c_e in the two first equations, leads to a closed system for (c_1, c_2):

$$\begin{pmatrix} E_1 - \frac{|V_{e1}|^2}{E_e - E} & \frac{V_{1e}V_{e2}}{E - E_e} \\ \frac{V_{2e}V_{e1}}{E - E_e} & E_2 - \frac{|V_{e2}|^2}{E_e - E} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} . \tag{12}$$

In this form, it is not too useful, as E appears on both side in a complicated way. But now assume you are only interested in the energy shifts of $|1\rangle$ and $|2\rangle$: the perturbation being weak ($|V_{1e}|, |V_{e2}| \ll \Delta E$), $E \sim E_{1,2} \ll E_e$. Hence Eq. (13) becomes:

$$\begin{pmatrix} E_1 - \frac{|V_{e1}|^2}{\Delta E} & -\frac{V_{1e}V_{e2}}{\Delta E} \\ -\frac{V_{2e}V_{e1}}{\Delta E} & E_2 - \frac{|V_{e2}|^2}{\Delta E} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \approx E \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} , \tag{13}$$

with $\Delta E \approx E_e - E_1 \approx E_e - E_2$. Therefore the elimination of c_e and the approximation $E \sim E_{1,2} \ll E_e$ lead to an effective hamiltonian restricted to the ground state manifold:

$$H_{\text{eff}} = \begin{pmatrix} E_1 - \frac{|V_{e1}|^2}{\Delta E} & -\frac{V_{1e}V_{e2}}{\Delta E} \\ -\frac{V_{2e}V_{e1}}{\Delta E} & E_2 - \frac{|V_{e2}|^2}{\Delta E} \end{pmatrix} , \tag{14}$$

with ΔE the energy of the gap between ground and excited states. This effective hamiltonian couples the two states $|1\rangle$ and $|2\rangle$, with an effective, second-order matrix element: $V_{\text{eff}} = -V_{1e}V_{e2}/\Delta E$. The energies are also shifted, as they should according to the discussion of Section 1. Moreover, as $|V_{1e}|, |V_{e2}| \ll \Delta E$, $|c_e| \ll 1$. The jargon used for what we have done here is: "obtaining an effective low-energy theory".

2.2 General case

The general procedure to obtain an effective hamiltonian, named the Schrieffer-Wolff transformation, is quite formal (see e.g. "Photons and Atoms", Cohen-Tannoudji, Dupont-Roc and Grynberg, Complement B_1). The result is however a direct generalization of the 3-level model we have just seen. For two states $|n\rangle$ and $|m\rangle$ in the lower manifold and many states $|k\rangle$ in the higher manifolds (see Fig. 2a), the second-order effective coupling between $|n\rangle$ and $|m\rangle$ is, with the gap energy $\Delta E_k \approx E_k - E_n \approx E_k - E_m$:

$$V_{\text{eff}}^{nm} = \frac{1}{2}\sum_k \langle n| \hat{V} |k\rangle \langle k| \hat{V} |m\rangle \left(\frac{1}{E_n - E_k} + \frac{1}{E_m - E_k} \right) \approx -\sum_k \frac{V_{nk}V_{km}}{\Delta E_k} . \tag{15}$$

2.3 Examples (solutions in Appendix)

F. Raman transition. Consider an atom with two degenerate ground-states $|1\rangle$ and $|2\rangle$ and an excited state $|e\rangle$ with an energy $\hbar\omega_0$. They are coupled to two laser beams (frequency ω, photon numbers N_1, N_2), with respective Rabi frequency Ω_{1e} and Ω_{2e}. We suppose $|\Delta| = |\omega - \omega_0| \gg \Omega_{ie}$. Calculate the coupling between the states $|1\rangle$ and $|2\rangle$.

G. Effective coupling in a double-well. Consider two sites a and b of a double well potential. We place two different particles 1 and 2 (e.g. a Rb and a Cs atom), each in the ground state of the wells. They can tunnel with an amplitude J, but placing two particles in the same well costs an energy $U \gg J$ due to their interaction. Calculate the amplitude of the coupling between the states $|1:a;2:b\rangle$ and $|2:a;1:b\rangle$.

H. Exchange interaction between two atoms via a cavity mode. We place two two-level atoms (states $|g\rangle, |e\rangle$, transition at ω_0) in an empty cavity defining an electromagnetic mode at frequency ω. The amplitude for an atom to drop or absorb a photon in/from the cavity is $\hbar\Omega$. If the two atoms are initially prepared in $|e,g\rangle$, in an empty cavity, show that they are coupled to the state $|g,e\rangle$, and calculate the transition amplitude for $|\omega - \omega_0| \gg \Omega$.

3 The variational method

If in many cases one does not know the exact solution of a problem, one may guess what it should look like. For example, a good guess for the ground state wavefunction of the finite depth square potential is a gaussian, parametrized by its width σ. The best approximation of the ground state is obtained by varying the width in order to minimize the energy calculated using the trial function, also called an “Ansatz”.

This way of proceeding, named the variational method, relies on the following consideration. Take a trial state $|\phi\rangle$ that you think is a reasonable form for the problem described by an hamiltonian H. Use it to compute the energy $E[\phi]$, which is a functional of the state:

$$E[\phi] = \frac{\langle\phi| H |\phi\rangle}{\langle\phi|\phi\rangle} \quad . \tag{16}$$

Then $E[\phi] \geq E_0$, the energy of the ground state. Indeed, the state $|\phi\rangle$ can be decomposed on the eigenstates $|\phi_n\rangle$ of H (even if you don't know them...): $|\phi\rangle = \sum_n c_n |\phi_n\rangle$. Assuming that $|\phi\rangle$ is normalized:

$$E[\phi] = \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2 = E_0 \ . \tag{17}$$

Hence minimizing $E[\phi]$ by varying $|\phi\rangle$, one obtains an upper bound of the ground-state energy. Let us consider a few examples (solutions in Appendix).

I. Ground state of the harmonic oscillator. Take $H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + m\omega^2 x^2/2$ and try the normalized wavefunction: $\phi_\sigma(x) = \exp(-\frac{x^2}{2\sigma^2})/(\sqrt{\pi}\sigma)^{1/2}$. The energy functional is:

$$E[\sigma] = \int_{-\infty}^{\infty} \phi_\sigma^*(x) H(x) \phi_\sigma(x)\, dx = \frac{\hbar^2}{4m\sigma^2} + \frac{1}{4} m\omega^2\sigma^2, \tag{18}$$

using the gaussian integrals: $\int_{-\infty}^{\infty} \exp(-x^2/\sigma^2)dx = \sqrt{\pi}\sigma$, and $\int_{-\infty}^{\infty} x^2 \exp(-x^2/\sigma^2)dx = \sqrt{\pi}\sigma^3/2$. Find the value of σ that minimizes the energy and the corresponding energy.

J. Size of a Bose-Einstein condensate. We consider a collection of bosonic atoms, all with the same wavefunction $\phi(x)$, placed in an harmonic potential. The atoms interact with each other, and the interaction potential has the form $g\phi(x)^2$. The total hamiltonian is therefore $H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + m\omega^2 x^2/2 + g\phi(x)^2$. Use a gaussian ansatz to estimate the ground state size of the wavefunction. Assume that the kinetic energy is negligible with respect to the interaction energy and give the condition under which this is valid.

K. Ground state of He atom. The hamiltonian for the two electrons of the He atoms restricted to the Coulomb interaction is

$$H = \frac{p_1^2}{2m} - \frac{2e^2}{r_1} + \frac{p_2^2}{2m} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \quad \text{with} \quad e^2 = \frac{q^2}{4\pi\epsilon_0}\ . \tag{19}$$

It has no analytical solution. One way to calculate the ground state is to use for each electron an ansatz wavefunction of the form $\psi_s(r) = \sqrt{Z^3/(\pi a_0^3)}\, \exp(-Zr/a_0)$, with Z a variable describing the screening of the nucleus by one of the electron for the other one. Calculations yield, with $|\phi_{12}\rangle = |\psi_{s1}, \psi_{s2}\rangle$ the two-electron wave function,

$$\langle\phi_{12}| \frac{p_1^2}{2m} - \frac{2e^2}{r_1} |\phi_{12}\rangle = \frac{Z^2e^2}{2a_0} - \frac{2Ze^2}{a_0} \quad \text{and} \quad \langle\phi_{12}| \frac{e^2}{r_{12}} |\phi_{12}\rangle = \frac{5Ze^2}{8a_0}\ . \tag{20}$$

Calculate the approximate ground state energy. The experimental value is -78.6 eV.

L. Linear combination of atomic orbitals. This method is widely used in chemistry to calculate the molecular orbitals of homo- or hetero-nuclear molecules. Consider for example the two identical atoms A and B (homonuclear case) described by a total Hamiltonian H, with atomic orbitals $|\phi_{A,B}\rangle$, such that $E_0 = \langle\phi_{A,B}| H |\phi_{A,B}\rangle$. Construct the molecular orbital by linear combination: $|\phi\rangle = c_A |\phi_A\rangle + c_A |\phi_B\rangle$. Calling $S = \langle\phi_A|\phi_B\rangle$ and $\beta = \langle\phi_A| H |\phi_B\rangle = \langle\phi_B| H |\phi_A\rangle$, use the variational method to find the coefficients c_A and c_B (supposed real), as well as the energies.

4 Time-dependent perturbation theory

Here, we want to know the time evolution of a system prepared at $t = 0$ in an initial eigenstate $|\phi_i\rangle$ of H_0 associated to the energy E_i (i.e., $H_0 |\phi_i\rangle = E_i |\phi\rangle_i$) after we turn on a perturbation $\hat{V}(t)$. The perturbation will couple $|\phi_i\rangle$ to other eigenstates $|\phi_n\rangle$, so that the state of the system at t is of the form

$$|\psi(t)\rangle = \sum_n c_n(t)\, e^{-i\frac{E_n}{\hbar}t}\, |\phi_n\rangle\ . \tag{21}$$

The time-evolution of the c_n's is ruled by the Schrödinger equation:

$$i\hbar\frac{d}{dt}\left|\psi(t)\right\rangle = (H_0 + \hat{V}(t))\left|\psi(t)\right\rangle \Rightarrow \dot{c}_n(t) = \frac{1}{i\hbar}\sum_k V_{nk}(t)e^{i\omega_{nk}t}\,c_k(t)\ , \tag{22}$$

with $\omega_{nk} = (E_n - E_k)/\hbar$ the Bohr frequencies. So far the expressions are exact, but the equations are difficult to solve as they are coupled.

Let us now make an approximation. At $t = 0$, $c_k(0) = \delta_{ki}$, and if the perturbations V_{nk} are weak, we expect that $c_i(t) \approx 1$. As a consequence, to first order in $V_{ni}/(\hbar\omega_{ni})$,

$$\dot{c}_n(t) \approx \frac{1}{i\hbar}V_{ni}(t)e^{i\omega_{ni}t} \quad \text{for} \quad n \neq i \Rightarrow c_n(t) \approx \frac{1}{i\hbar}\int_0^t V_{ni}(t')e^{i\omega_{ni}t'}\,dt'\ . \tag{23}$$

Hence the transition amplitude from i to n is the Fourier transform of the matrix element coupling the two states, and the corresponding probability is:

$$P_{i\to n}(t) \approx \frac{1}{\hbar^2}\left|\int_0^t V_{ni}(t')e^{i\omega_{ni}t'}\,dt'\right|^2\ . \tag{24}$$

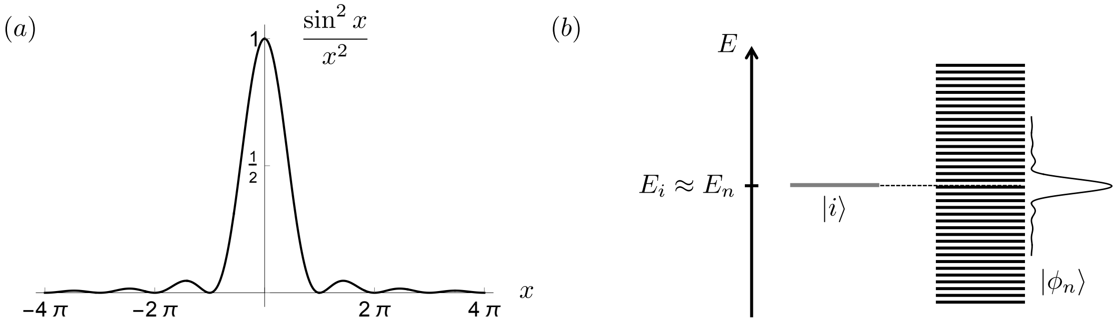

Figure 3: *Time-dependent perturbation theory. (a) Function* $\sin^2 x/x^2$ *involved in the transition probability. (b) A single state* $|i\rangle$ *coupled to a quasi-continuum of states* $|\phi_n\rangle$*. Only the states* $|\phi_n\rangle$ *with an energy close to* E_i *contribute significantly to the transition.*

Constant perturbation. We assume first that $\hat{V}$ is independent of time. Then,

$$P_{i\to n}(t) \approx \frac{4|V_{ni}|^2}{(\hbar\omega_{ni})^2}\sin^2\left(\frac{\omega_{ni}t}{2}\right)\ . \tag{25}$$

The transition probability oscillates as a function of t at the Bohr frequency ω_{ni}, with an amplitude $4|V_{ni}|^2/(\hbar\omega_{ni})^2$. The validity of the perturbation approach is consistent with $|V_{ni}| \ll \hbar\omega_{ni}$. Also, fixing the duration T of the perturbation, the transition probability, of the form $\sin^2 x/x^2$, is maximal for $E_n = E_i$ (see Fig. 3a), and $P_{i\to n}^{\max} = |V_{ni}|^2T^2/\hbar^2$. This is valid at short times, for $T \ll \hbar/|V_{ni}|$.

Sinusoidal perturbation. Frequently, the perturbation has the form $\hat{V}\cos\omega t$ as for a laser or microwave field sent onto an ensemble of atoms, for example. Then

$$P_{i\to n}(t) \approx \frac{|V_{ni}|^2}{4\hbar^2}\left|\frac{e^{i(\omega+\omega_{ni})t}-1}{\omega+\omega_{ni}} + \frac{e^{i(\omega_{ni}-\omega)t}-1}{\omega_{ni}-\omega}\right|^2\ . \tag{26}$$

In the near-resonant case, $|\omega - \omega_{ni}| \ll \omega + \omega_{ni}$, and

$$P_{i\to n}(T) \approx \frac{|V_{ni}|^2}{\hbar^2} \frac{\sin^2[(\omega - \omega_{ni})T/2]}{(\omega - \omega_{ni})^2} \ . \tag{27}$$

Once again, the transition probability is the largest when energy is conserved, i.e., $E_n = E_i + \hbar\omega$, and the width of the resonance fulfills $\Delta\omega \times T \sim 1$.

5 “Fermi Golden rule”

Let us calculate the probability $P(T)$ that the systems leaves the state $|\phi_i\rangle$, irrespective of the state $|\phi_n\rangle$ it ends up in. The final states being all orthogonal with each other, we sum the probabilities

$$P(T) = \sum_n P_{i\to n}(T) = \sum_n \frac{4|V_{ni}|^2}{\hbar^2} \frac{\sin^2[\omega_{ni}T/2]}{\omega_{ni}^2} \ , \tag{28}$$

for the case of a constant perturbation.

We consider now the situation where many states $|\phi_n\rangle$ with energy $E_n \approx E_i$ are contained within the linewidth $\Delta\omega \sim 1/T$ of the excitation (see Fig. 3b). This situation is called a quasi-continuum and allows one to replace the sum by an integral, the energy being considered as a continuous variable:

$$\sum_n \to \int \rho(E_n) dE_n \ , \tag{29}$$

where $\rho(E)$ is called the density of state and measures the number of states with an energy between E and $E + dE$. Thus

$$P(T) = \int dE_n \, \rho(E_n) \frac{4|V_{ni}|^2}{\hbar^2} \frac{\sin^2(\omega_{ni}T/2)}{\omega_{ni}^2} \ . \tag{30}$$

In most cases, the density of state is a slowly varying function with E, and so is the matrix element $V_{ni} = V_{fi}$. They may therefore be taken out of the integral, as the $\sin^2 x/x^2$ function is peaked around E_i:

$$P(T) = \frac{2|V_{fi}|^2 T}{\hbar} \rho(E_i) \int \frac{\sin^2(\omega_{ni}T/2)}{(\omega_{ni}T/2)^2} \, d\left(\frac{E_n T}{2\hbar}\right) \ . \tag{31}$$

A change in variable $x = \omega_{ni}T/2$ and the use of $\int_{-\infty}^{\infty} \sin^2 x/x^2 \, dx = \pi$ leads to the rate of transition out of the initial state to a final state with energy $E_f = E_i$.

$$\Gamma = \frac{P(T)}{T} = \frac{2\pi}{\hbar} |V_{fi}|^2 \rho(E_i) \ . \tag{32}$$

This last formula is called the ”Fermi golden rule”. It is used in many contexts when an initial state is coupled to a continuum, such as in a collision between two particles, the decay of a nucleus or an atom, the coupling of electrons to phonons in a crystal...

Warning note: the Fermi rule should *not* be learned by heart! You should re-derive its expression for your case, starting from Eqs. (25,26). For example, had we considered the sinusoidal perturbation $\hat{V}\cos\omega t$, we would have obtained instead of Eq. (32):

$$\Gamma = \frac{P(T)}{T} = \frac{\pi}{2\hbar}|V_{fi}|^2\rho(E_i + \hbar\omega) \ . \tag{33}$$

Besides, we used above the energy as the continuous variable, but in other situations, you may have to use variables such as the wavevector of a photon emitted by an atom, or of a phonon in a solid, or an angular momentum associated to the rotation of a molecule,... However, the structure of the transition rate will always look the same:

$$d\Gamma \sim \frac{2\pi}{\hbar} \times |V_{if}|^2 \times \delta(E_i - E_f) \times dQ \ . \tag{34}$$

Appendix: solutions of the problems

A. Zeeman effect on an atom. The energy of a state $|n, j, m_j\rangle$ is E_n in the absence of field. The Hamiltonian of a magnetic moment placed in a magnetic field $\mathbf{B}$ is $H = -\boldsymbol{\mu}\cdot\mathbf{B} = -\gamma\hat{J}_zB$. Hence, the first order shift in energy is $\Delta E^{(1)} = -\gamma B m_j$ for a state $|n, j, m_j\rangle$. The total energies are thus $E_n - \gamma B m_j$, with $|m_j| \leq j$. Valid as long as $\gamma B j \ll E_{n+1} - E_n$.

B. Non-harmonic oscillator. The energy shift of $|n = 0\rangle$ is, to first order, $\Delta E^{(1)} = \langle n = 0|\, g\hat{x}^4\, |n = 0\rangle = g x_0^4 \langle n = 0|\, (\hat{a} + \hat{a}^+)^4\, |n = 0\rangle = 3g x_0^4$.

C. Stark shift of an atom and polarizability. The wavefunctions of the lowest states are ψ_{1s}, ψ_{2s} and ψ_{2p}. Due to symmetry, the matrix elements of $\hat{z}$ are non zero only between states of opposite parity, such as $s(l = 0)$ and $p(l = 1)$. Hence, $\langle\psi_{1s}|\, \hat{z}\, |\psi_{1s}\rangle = 0$ and $\Delta E^{(1)}_{\text{gs}} = 0$. The second order shift of the ground state $1s$ is

$$\Delta E^{(2)}_{\text{gs}} = \frac{d_{sp}^2 E^2}{E_{1s} - E_{2p}} \quad \text{with} \quad d_{sp} = \langle\psi_{1s}|\, q\hat{z}\, |\psi_{2p}\rangle \ .$$

As $E_{1s} < E_{2p}$, $\Delta E^{(2)}_{\text{gs}} = -\epsilon_0\alpha E^2/2 < 0$, with $\alpha = 2d_{sp}^2/(\epsilon_0|E_{1s} - E_{2p}|)$. The ground-state is modified as:

$$|\tilde{\psi}_{1s}\rangle = |\psi_{1s}\rangle - \frac{d_{sp}E}{E_{1s} - E_{2p}}\, |\psi_{2p}\rangle \ .$$

The average dipole is $\langle d\rangle = \langle\tilde{\psi}_{1s}|\, q\hat{z}\, |\tilde{\psi}_{1s}\rangle = \epsilon_0\alpha E$.

D. Van der Waals interaction between two atoms. We consider the two-atom state $|ns, ns\rangle$, where each atom is in the state $|ns\rangle$. The dipolar interaction hamiltonian H_{I} couples it to $|np, np\rangle$ separated by an energy $2\hbar\omega_0$. The first order shift is again null, and the second order shift is:

$$\Delta E^{(2)}_{\text{ss}} = \frac{|\, \langle np, np|\, H_{\text{I}}\, |ns, ns\rangle\, |^2}{E_{ss} - E_{pp}} = -\left(\frac{d_{sp}^2}{4\pi\epsilon_0 R^3}\right)^2 \frac{1}{2\hbar\omega_0} \ .$$

It is of the form $-C_6/R^6$, and corresponds to the van der Waals interaction between two neutral particles.

E. Light-shift induced by a laser. The two states $|g, N\rangle$ and $|e, N-1\rangle$ are separated in energy by $E_{g,N} - E_{e,N-1} = \hbar(\omega - \omega_0)$. Thus, $\Delta E^{(2)}_{g,e} = \pm\hbar\Omega^2/\Delta$.

F. Raman transition. The system involves three partners: the atom and the two lasers, and the relevant states are thus $|1, 2, e; N_1; N_2\rangle$. The state $|1; N_1; N_2\rangle$ is coupled to the state $|e; N_1 - 1; N_2\rangle$ by the first laser (absorption of a photon). This last state is then coupled to $|2, N_1 - 1, N_2 + 1\rangle$ by the second laser (emission of a photon in the laser mode). The states $|1; N_1; N_2\rangle$ and $|2, N_1 - 1, N_2 + 1\rangle$ are still degenerate, and separated in energy from the state $|e; N_1 - 1; N_2\rangle$ by $\hbar(\omega_0 - \omega)$. The effective coupling between the states $|1\rangle$ and $|2\rangle$ is thus $\Omega_{1e}\Omega_{2e}/|\Delta|$.

G. Effective coupling in a double-well. The swap of the particles involves, for example, the first particle to tunnel onto site b (amplitude J), leaving site a empty. The corresponding state $|0 : a; 1, 2 : b\rangle$ has an energy U above the initial state $|1 : a; 2 : b\rangle$ (assuming $U > 0$). Then, the second particle tunnels onto site a leading to the state $|2 : a; 1 : b\rangle$ (amplitude J). The amplitude of this coupling is thus J^2/U. The swap can also start with the second particle hopping first onto site a. This gives the same amplitude J^2/U, and thus the total amplitude of the coupling is $2J^2/U$.

H. Exchange interaction between two atoms via a cavity mode. We have to consider the system {atom 1, atom 2, field}. The initial state is $|e, g, n = 0\rangle$, with n the number of photons in the cavity. The first atom emits a photon in the cavity mode (frequency ω) leading to the intermediate state $|g, g, n = 1\rangle$ with an energy difference with respect to the first state $\hbar(\omega - \omega_0)$. The photon gets reabsorbed by the second atom, leading to $|g, e, n = 0\rangle$. The amplitude of the coupling when $|\omega - \omega_0| \gg \Omega$ is thus $\hbar\Omega^2/|\omega - \omega_0|$.

I. Ground state of the harmonic oscillator. Solving $dE[\sigma]/d\sigma = 0$ yields $\sigma_{\min} = \sqrt{\hbar/m\omega}$, and the corresponding energy $E_{\min} = \hbar\omega/2$. In this case, we find the exact answer, just because we have done the good guess! Had we, for example, used for the trial function a lorentzian: $\phi_a(x) \sim 1/(x^2 + a^2)$, we would have found $E_{\min} = \hbar\omega/\sqrt{2} \geq E_0$.

J. Size of a Bose-Einstein condensate. Using a gaussian Ansatz $\phi_\sigma(x)$ and the gaussian integrals given for the previous example, one finds:

$$\langle H\rangle = \frac{\hbar^2}{4m\sigma^2} + \frac{1}{4}m\omega^2\sigma^2 + g\int_{-\infty}^{\infty}\phi(x)^4 dx = \frac{\hbar^2}{4m\sigma^2} + \frac{1}{4}m\omega^2\sigma^2 + \frac{g}{\sqrt{2\pi}\sigma} \ .$$

Neglecting the kinetic energy term and solving $d\langle H\rangle/d\sigma = 0$ gives $\sigma_{\mathrm{m}} = (\sqrt{\frac{2}{\pi}}\frac{g}{m\omega^2})^{1/3}$. The assumption is valid when the ratio of the kinetic energy to the interaction energy is negligible: $\hbar^2/(m\sigma_{\mathrm{m}}^2) \ll (g/\sigma_{\mathrm{m}})$ or equivalently $g/\hbar \gg \sqrt{\hbar\omega/m}$.

K. Ground state of He atom. Using the expressions given in the text

$$\langle H \rangle = 2\left(\frac{Z^2e^2}{2a_0} - \frac{2Ze^2}{a_0}\right) + \frac{5Ze^2}{8a_0} = \frac{e^2}{2a_0}\left(2Z^2 - \frac{27}{4}\right) .$$

Minimizing with respect to Z gives $Z_{\mathrm{m}} = 27/16 < 2$: the second electron screens partially the charge $Z_{\mathrm{n}} = 2$ of the nucleus. The corresponding ground state energy is $-2 \times (27/16)^2 \times (e^2/2a_0) = -77.5$ eV. This value is much closer to the measured one than if we had neglected the interaction between electrons (we would have found $-2 \times 4 \times 13.6 = 108.8$ eV).

L. Linear combination of atomic orbitals. The energy functional is

$$E[c_A, c_B] = \frac{\langle\phi|\, H \,|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{(c_A^2 + c_B^2)E_0 + 2c_Ac_B\beta}{c_A^2 + c_B^2 + 2c_Ac_BS} .$$

The minimization implies solving the set of two coupled equation $\frac{\partial E}{\partial c_A} = 0, \frac{\partial E}{\partial c_B} = 0$. This yields the equation $(c_A^2c_B - c_B^3)(E_0S - \beta) = 0$, hence $c_A = \pm c_B$. The normalisation condition $\langle\phi|\phi\rangle = 1$ gives $c_{A,B} = \pm 1/\sqrt{2(1 \pm S)}$, and the corresponding energies are $E_\pm = (E_0 \pm \beta)/(1 \pm S)$.