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Perturbation Theory

A Introductory Remarks

If we have a Hamiltonian for which we cannot find exact eigenvalues and eigenvectors, we can in principle use the technique employed for the asymmetric rotator for more challenging problems. If for the moment $|n\rangle$ is shorthand for the eigenvectors for a complete set of commuting operators, *including* the Hamiltonian in question, and $|\alpha\rangle$ is shorthand for the eigenvectors of another complete set of commuting operators, spanning the same subspace of Hilbert space, but now *including* a simpler Hamiltonian, H_0, for which we *do* know the eigenvalues and eigenvectors, we can expand the unknown eigenvectors $|n\rangle$ in terms of the known $|\alpha\rangle$. From a knowledge of the matrix elements, $\langle\alpha'|H|\alpha\rangle$, we can in principle diagonalize the matrix in this basis for H_0 to find the eigenvalues and eigenvectors for the needed H. The difficulty, of course, is that in general this matrix will be infinite-dimensional. With modern computers, however, it may be possible to diagonalize this matrix in an $N \times N$ limit, where N is taken to be a large number, and then test the possible convergence as N grows even larger. This method will be particularly successful if H differs from a known H_0 by terms that can be classified by a parameter of smallness, λ, with $\lambda \ll 1$. Then, we can study the "corrections" to the eigenvalues and eigenvectors in a very systematic way as a power series in λ. This will be the first detailed study of the next chapter, which will include:

(1) stationary-state or time-independent perturbation theory,
(a) Rayleigh–Schrödinger expansion,
(b) Wigner–Brillouin expansion.

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This study will be in contrast to time-dependent perturbation theory, which will be covered in a later chapter; where we will make a similar expansion of the time-dependent integral of eq. (13) of Chapter 19. Other approximation techniques, also to be covered in later chapters, are the WKB or semiclassical approximation and variational methods.

The WKB approximation will be treated only after a long excursion on angular momentum theory, Part III of the course. Variational methods useful for the n electron atom will be discussed in Part IV of the course on systems of identical particles.

B Transition Probabilities

Before proceeding with stationary-state perturbation theory, it will be advantageous to give a very brief first discussion of transition probabilities to answer the question: What is the probability an atomic system in an excited eigenstate, E_n, will make a transition to a lower state, E_m, through the spontaneous emission of a photon? To answer this question in a rigorous way, we will have to study both the atomic system and the electromagnetic field quantum mechanically; i.e., we would have to quantize the electromagnetic field and then study the interaction of the quantized electromagnetic field (photon) with the atomic system. Because we will save the study of time-dependent perturbation theory for a later chapter, we will do this in a rigorous fashion then. To have a formula for the transition probability for the spontaneous emission of a photon, however, let us give a very brief "plausibility" argument for the transition probability formula now. This will actually be the historically first (the so-called Bohr correspondence principle) argument for this formula. (Keep in mind, however, the rigorous derivation will come later. Historically, it also came later with a famous paper by Dirac on the quantization of the electromagnetic field.)

The Bohr argument goes as follows: Classically, a charged particle in motion will emit electromagnetic radiation only if the particle is accelerated. Quantitatively, the *classical* result is given by the Larmor formula, which calculates the energy *loss* per unit time of the charged particle (or a system of N charged particles) to the emission of electromagnetic radiation (in c.g.s. units),

$$-\frac{dE}{dt} = \frac{2e^2}{3c^3}\vec{a}^2 \qquad \text{or} \qquad -\frac{dE}{dt} = \frac{2}{3c^3}\sum_{i=1}^{N}\left(e_i\vec{a}_i\right)^2, \tag{1}$$

where $\vec{a}_i$ is the acceleration vector of the i^{th} particle with charge e_i. The classical recipe for calculating this energy loss for a system of N moving particles involves the Fourier time analysis for the three components of the electric dipole moment

$$\sum_{i=1}^{N} e_i x_i = \sum_{n}^{\infty} \mu_n^{(x)}\left(e^{in\omega t} + e^{-in\omega t}\right),$$

$$\sum_{i=1}^{N} e_i y_i = \sum_{n}^{\infty} \mu_n^{(y)} \left(e^{in\omega t} + e^{-in\omega t}\right),$$
$$\sum_{i=1}^{N} e_i z_i = \sum_{n}^{\infty} \mu_n^{(z)} \left(e^{in\omega t} + e^{-in\omega t}\right), \tag{2}$$

assuming for the moment the time-dependent functions are real. Then, according to classical theory, the frequencies radiated are the classical mechanical frequency and its overtones, $\nu = \omega/2\pi$, and $n\nu$ (or in the case of multiple-periodic systems, the classical frequencies and their overtones or combination tones, $n_1\nu_1 + n_2\nu_2$, etc.). Taking the second time derivatives of the x_i, y_i, z_i of eq. (2), the classically predicted energy loss to the n^{th} *overtone* (time-averaged over one cycle) would have been

$$-\overline{\left[\frac{dE}{dt}\right]}_{n\nu} = \frac{2}{3c^3} \times 2(n\omega)^4 \left(\left(\mu_n^{(x)}\right)^2 + \left(\mu_n^{(y)}\right)^2 + \left(\mu_n^{(z)}\right)^2\right). \tag{3}$$

Of course, this classical result is incorrect. This is what troubled Niels Bohr from 1913 to 1925. First, this result does not predict the observed frequencies. The hydrogen spectrum is *not* a fundamental frequency and its n overtones. Even worse, this classical result predicts the frequencies should change with time. As the system loses energy and the mechanical energy becomes more negative, the Kepler frequencies (or the Bohr "1913 frequencies") would increase with time; the electron would spiral in to the proton and suffer a catastrophe in a time of the order of 10^{-8} seconds. Bohr argued, however, the classically predicted frequency, $n\omega$, should be replaced by the Bohr frequency, ω_{nm}, and the classically predicted Fourier coefficients, $\mu_n^{(j)}$, should be replaced by a two-index quantity, $\mu_{nm}^{(j)}$, which he identified with the Heisenberg matrix element. Thus,

$$\begin{array}{lll}
\text{classical} & n\nu \to (E_n - E_m)/h & \text{(Bohr)}, \\
\text{classical} & \mu_n^{(x)} \to \langle n|\mu_x|m\rangle & \text{(Heisenberg)}, \\
\text{classical} & \mu_n^{(y)} \to \langle n|\mu_y|m\rangle & \text{(Heisenberg)}, \\
\text{classical} & \mu_n^{(z)} \to \langle n|\mu_z|m\rangle & \text{(Heisenberg)}.
\end{array} \tag{4}$$

This argument is the Bohr correspondence principle, which yields the result

$$-\left[\frac{dE}{dt}\right]_{\nu_{nm}} = \frac{64\pi^4}{3c^3}\nu_{nm}^4 \left[|\langle n|\mu_x|m\rangle|^2 + |\langle n|\mu_y|m\rangle|^2 + |\langle n|\mu_z|m\rangle|^2\right], \tag{5}$$

where the operators are $\mu_x = \sum_i^N e_i x_i$, and so on. To convert this principle to a transition probability, introduce the "Einstein A,"

$$-\left[\frac{dE}{dt}\right]_{\nu_{nm}} = h\nu_{nm} A_{n\to m} N_n, \tag{6}$$

where $h\nu_{nm}$ is the energy of the emitted photon, $A_{n\to m}$, gives the probability per unit time for the spontaneous emission of a photon with this frequency, and N_n is the number of atoms in the initial state, n. The transition probability per second the atom makes a transition from an excited state, n, to a lower state, m, is therefore

given in terms of the matrix elements of the three components of the electric dipole moment operator by

$$A_{n\to m} = \frac{64\pi^4}{3hc^3}\nu_{nm}^3\left[|\langle n|\mu_x|m\rangle|^2 + |\langle n|\mu_y|m\rangle|^2 + |\langle n|\mu_z|m\rangle|^2\right]. \tag{7}$$

If the matrix elements of the three electric dipole moment components are all zero, the transition is "forbidden." The correspondence principle argument then gives the correct result. A rigorous derivation will be given in a later chapter, when we shall quantize the electromagnetic field and introduce the interaction between the quantized electromagnetic field (photons) and the isolated atomic system. The above electric dipole result, however, is only the dominant term in an expansion involving a series in powers of a/λ, where a gives the size of the atomic system and λ is the wavelength of the emitted photon. Higher order terms will involve matrix elements of magnetic moment operators, electric quadrupole moment operators, and even higher magnetic and electric multipole moments. In nuclei, these higher order terms are often important.

Finally, we make a remark about induced absorption and emission processes. If the atomic system is in a beam or a bath of photons, the probability for induced absorption and emission processes is given by the "Einstein B"s and by $\rho(\nu_{nm})$, the energy density of the electromagnetic radiation (photon beam). Through his study of the black-body radiation spectrum, Einstein found the relation

$$B_{m\to n} = B_{n\to m} = \frac{c^3}{8\pi h\nu_{nm}^3}A_{n\to m}, \tag{8}$$

where the probability per unit time of an induced absorption process is

$$\rho(\nu_{nm})B_{m\to n}N_m, \tag{9}$$

and the probability per unit time of an induced emission process is

$$\rho(\nu_{nm})B_{n\to m}N_n, \tag{10}$$

where $\rho(\nu_{nm})$ is the energy per unit volume of the photon beam at the transition frequency, and N_n and N_m are the number of atoms in state n and m, respectively.

Problems

27. Find the lifetime τ in seconds of the 2p state of the hydrogen atom

$$\tau = \frac{1}{A_{2p\to 1s}},$$

where $A_{2p\to 1s}$ is the Einstein A coefficient. Assume the three substates with $m = 0, \pm 1$ are populated with equal probability initially.

28. For the diatomic molecule rigid rotator, the space-fixed components of the electric dipole moment operator are

$$\mu_x^{(\mathrm{el.})} = \mu_e \sin\theta\cos\phi, \qquad \mu_y^{(\mathrm{el.})} = \mu_e \sin\theta\sin\phi, \qquad \mu_z^{(\mathrm{el.})} = \mu_e \cos\theta,$$

where μ_e is the permanent electric dipole moment of the molecule, oriented along the molecular symmetry axis. (Homonuclear diatomic molecules, such as H_2 or N_2, have no permanent electric dipole moment. Their pure rotational transitions can therefore only be seen in Raman spectroscopy.)

Recall the rotational energies and wave functions are given by

$$E_J = \frac{\hbar^2}{2I_e} J(J+1), \quad \text{with } I_e = \mu r_e^2, \qquad \psi_{JM}(\theta, \phi) = Y_{JM}(\theta, \phi).$$

Give a general formula for the energy loss per second for an emission line for a transition $J \to (J-1)$, assuming the molecule is in a gaseous sample in thermal equilibrium at temperature T, where the number of molecules in the state with energy E_J is

$$N_J = \frac{(2J+1)e^{-(E_J/kT)}}{\sum_J (2J+1)e^{-(E_J/kT)}} N_{\text{total}} \approx \frac{\hbar^2}{2I_e kT}(2J+1)e^{-(E_J/kT)} N_{\text{total}}.$$

For example, for the HBr molecule with $r_e = 1.414 \times 10^{-8}$ cm, and $\mu_e = e(0.17 \times 10^{-8}$ cm), make an estimate for the $J = 3 \to 2$ transition in terms of the number of photons emitted per second. Your numerical answer should explain why such spectra are observed as absorption spectra rather than emission spectra. That is, the spontaneous emission process is very unlikely, so diatomic molecule rotational transitions are observed by utilizing the stimulated absorption and emission process for incident radiation of the appropriate frequency in the far infrared or microwave region. To come to the same conclusion, also calculate the lifetime in seconds of the first excited rotational state, with $J = 1$, and compare this result for the HBr molecule with the result of problem 27 for the first excited state of the hydrogen atom.