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1 Preface

A less known aspect of the quasi-classical approximation to quantum-mechanical motion is presented in this book.

As it is well known, the quasi-classical approximation exists whenever the relevant amount of mechanical action is large in comparison with the quantum of action $\hbar$ (Planck's constant). This happens at high values of energy, associated with large quantum numbers, where the wavefunction exhibits many oscillations in time and space. Under these circumstances, Bohr's correspondence principle holds and the quantum-mechanical motion is approaching the classical limit. According to Dirac, the quantum-mechanical commutators become the classical Poisson brackets in this case. Similarly, in the limit $\hbar \rightarrow 0$, the quantum waves may exhibit a trajectory, like the wave rays in the approximation of the geometrical optics, and the Bohr-Sommerfeld quantization conditions of the Old Quantum Mechanics (related to the adiabatic invariants) are valid; this is known as the Jeffreys-Wentzel-Kramers-Brillouin (JWKB) approximation. Moreover, in the same conditions, a superposition of waves yields wavepackets localized in space, with sharp values in energy (extended in time), which mimic classical particles; moving with the group velocity and obeying the classical equations of motion, according to Ehrenfest.

All these aspects refer mainly to stationary states. The investigations presented in this book refer especially to the quasi-classical aspect of the quantum-mechanical transitions (quantum jumps).

The starting point of the matters discussed here is the equation of motion

$$\dot{O}(t) = \frac{i}{\hbar}[H, O(t)] \tag{1.1}$$

for Heisenberg's representation $O(t) = e^{\frac{i}{\hbar}Ht}Oe^{-\frac{i}{\hbar}Ht}$ for operators O, where H is the time-independent hamiltonian; in the energy representation, equation (1.1) reads

$$\dot{O}_{nm} = \frac{i}{\hbar}(E_n - E_m)O_{nm} \ , \tag{1.2}$$

where E_n, E_m are the energies of the states n, m, or

$$\dot{O}_{nm} = i(\omega_n - \omega_m)O_{nm} \ , \tag{1.3}$$

where $\omega_{n,m} = E_{n,m}/\hbar$. For large n, m (E_n,E_m), where small deviations $s = m - n$ are relevant, we may write approximately $\omega_m = \omega_{n+s} = \omega_n + s(\partial\omega_n/\partial n)$ and, denoting $\omega_s = s(\partial\omega_n/\partial n)$ for fixed n, we get

$$\dot{O}_{n,n+s} = -i\omega_s O_{n,n+s} \ . \tag{1.4}$$

On the other hand, the matrix elements $O_{n,n+s}$ of the dynamical variables vanish rapidly with increasing s and depend slightly on n so we may approximate $O_{n,n+s}$ by $O_{n,n+s} \simeq O_s$.[1] Therefore, we have

$$\dot{O}_s = -i\omega_s O_s \ . \tag{1.5}$$

With $O_s = O_s^{(1)} + iO_s^{(2)}$ we get $\dot{O}_s^{(1)} = \omega_s O_s^{(2)}$, $\dot{O}_s^{(2)} = -\omega_s O_s^{(1)}$ and

$$\ddot{O}_s^{(1)} = -\omega_s^2 O_s^{(1)} \ , \ \ddot{O}_s^{(2)} = -\omega_s^2 O_s^{(2)} \ . \tag{1.6}$$

This is the classical equaton of motion of a free harmonic oscillator with the eigenfrequency ω_s. The classical quantity corresponds either to $O_s^{(1)}$ or $O_s^{(2)}$. This observation opens the possibility to approximate the quantum-mechanical operators by classical harmonic oscillators in the quasi-classical conditions. The effective hamiltonian which governs the motion of $O_s^{(1,2)}$ is

$$H_{eff} = \frac{1}{2m}P_s^{(1,2)2} + \frac{1}{2}m\omega_s^2 O_s^{(1,2)2} \ , \tag{1.7}$$

where $P_s^{(1,2)}$ is the momentum associated to the dynamical variable $O_s^{(1,2)}$. We may drop out the suffix s and the upper indices 1, 2 and write equations (1.6) as

$$\ddot{O} + \omega_0^2 O = 0 \ , \tag{1.8}$$

[1] Angular coordinates like φ or θ of the rotation motion are an exception; rather their trigonometric functions like $\cos\varphi$, $\cos\theta$ are representative for the assertion made in the text.

where we introduced the notation $\omega_0 = \omega_s$. Equation (1.8) has a twofold nature: classical and quantum-mechanical. On one hand, it is the classical equation of a harmonic oscillator; on the other hand, it contains the oscillator eigenvalue ω_0 which is the difference $\omega_0 = \omega_s = (E_m - E_n)/\hbar$ of two quantum-mechanical frequencies (two energy levels), which may be involved in a quantum transition. For this reason, and taking into account the conditions used in deriving it, we call this equation a quasi-classical equation of motion.

In the presence of an external interaction H_{int} equation (1.5) acquires an additional term $\dot{O}_s^{cl}$,

$$\dot{O}_s = -i\omega_s O_s + \dot{O}_s^{cl} \quad , \tag{1.9}$$

which denotes the part in the time derivative of the classical quantity O that arises from the external interaction; the harmonic-oscillator quasi-classical equation of motion becomes

$$\ddot{O} + \omega_0^2 O = \left(\frac{\partial}{\partial t} \dot{O}^{cl} \right)_{int} \quad ; \tag{1.10}$$

the *rhs* of this equation is a generalized force, the suffix *int* indicating explicitly that this force is generated exclusively by the external interaction. The calculation of the generalized force is performed by means of the Poisson brackets:

$$\left(\frac{\partial}{\partial t} \dot{O}^{cl} \right)_{int} = \{\{O, H_{eff}\}, H_{int}\} + +\{\{O, H_{int}\}, H_{eff}\} \quad , \tag{1.11}$$

where we retain only the first-order contribution of the interaction hamiltonian. Indeed, we are interested in the particular solution of equation (1.10), which, under these circumstances, has the character of a small perturbation; consequently, it is convenient to use the symbol δO in equation (1.10),

$$\delta\ddot{O} + \omega_0^2 \delta O = \left(\frac{\partial}{\partial t} \dot{O}^{cl} \right)_{int} \quad , \tag{1.12}$$

indicating the variation of the quantity O for small changes in the quantum numbers ($s \ll m$). If δO appears in the generalized force, it should be neglected for consistency. If, for some special forms of

H_{int}, the variable O or/and its conjugate momentum P appear in the generalized force, then approximate schemes should be used, which depend on the specific problem. For other special prblems there may not exist a classical hamiltonian of interaction, but only equations of motion (for instance, for magnetic moments); in that cases, the generalized force is computed according to the basic meaning of the time derivative.

One of the most simple forms for the interaction hamiltonian is

$$H_{int} = fO\cos\omega t \ , \tag{1.13}$$

which corresponds to the interaction of a harmonic oscillator with an external field of strength f and frequency ω. The quasi-classical equation of motion reads

$$\delta\ddot{O} + \omega_0^2\delta O + 2\alpha\delta\dot{O} = -\frac{f}{m}\cos\omega t \tag{1.14}$$

($\dot{O} = P/m$, $\dot{P} = -\omega_0^2 O - f\cos\omega t$), where the friction (damping) term $2\alpha\delta\dot{O}$ is introduced. The particular solution of this equation is

$$\begin{gathered} \delta O = a\cos\omega t + b\sin\omega t \ , \\ a = \tfrac{f}{2m\omega_0}\tfrac{\omega-\omega_0}{(\omega-\omega_0)^2+\alpha^2} \ , \ b = -\tfrac{f}{2m\omega_0}\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \ , \end{gathered} \tag{1.15}$$

for ω near ω_0. This is a typical resonance solution. From equation (1.14) we get

$$\frac{d}{dt}\left(\frac{1}{2}m\delta\dot{O}^2 + \frac{1}{2}m\omega_0^2\delta O^2\right) + 2\alpha m\delta\dot{O}^2 = -f\delta\dot{O}\cos\omega t \ , \tag{1.16}$$

which shows that

$$\delta P_{osc} = -\overline{f\delta\dot{O}\cos\omega t} = -\frac{1}{2}fb\omega \tag{1.17}$$

is the mean rate of energy absorption (dissipated power) of the oscillator. Making use of equation (1.15) we get

$$\begin{gathered} \delta P_{osc} = -\tfrac{1}{2}fb\omega \simeq \tfrac{f^2}{4m}\tfrac{\alpha}{(\omega-\omega_0)^2+\alpha^2} \rightarrow \\ \rightarrow \tfrac{\pi f^2}{4m}\delta(\omega_0 - \omega) \ , \ \alpha \rightarrow 0^+ \ . \end{gathered} \tag{1.18}$$

The power given by equation (1.18) should be compared with the mean power absorbed by the oscillator in quantum transitions. For the interaction hamiltonian $H_{int} = h\cos\omega t$ the amplitude of transition $n \rightarrow k$ is given by

$$c_{kn} = -\frac{h_{kn}}{2\hbar}\frac{e^{i(\omega_{kn}-\omega)t+\alpha t}}{\omega_{kn}-\omega-i\alpha} \ ; \tag{1.19}$$

the rate of transition is

$$\begin{aligned} \frac{\partial|c_{kn}|^2}{\partial t} &= \frac{|h_{kn}|^2}{2\hbar^2}\frac{\alpha}{(\omega_{kn}-\omega)^2+\alpha^2} \rightarrow \\ &\rightarrow \frac{\pi|h_{kn}|^2}{2\hbar^2}\delta(\omega_{kn}-\omega) \ , \ \alpha \rightarrow 0^+ \end{aligned} \tag{1.20}$$

and the absorbed power is

$$P = \frac{\pi\left|h_{kn}\right|^2}{2\hbar}\omega_{kn}\delta(\omega_{kn}-\omega) \ . \tag{1.21}$$

For $h = fO$, the matrix elements $O_{n+1,n} = \sqrt{\hbar(n+1)/2m\omega_0}$ of the harmonic oscillator and $\omega_{kn} = \omega_{n+1} - \omega_n = \omega_0$ we get

$$P = \frac{\pi f^2}{4m}(n+1)\delta(\omega_0-\omega) \ ; \tag{1.22}$$

we can see that $\delta P = \delta P_{osc}$ given by equation (1.18) for large n.

For other, simple quantum-mechanical motions the difference between the two powers is only a numerical factor; the planar rotator and the spatial rotator (spherical top) analyzed in this book illustrate this point. The difference indicates the deviation of the quantum-mechanical motion from the motion of the harmonic oscillator; it originates in the approximations made in deriving the quasi-classical equation of motion given by equation (1.12).

The extension of the quasi-classical equation of motion to condensed matter exhibits a few particularities. Because of the residual interactions the quantum-mechanical motion in condensed matter has certain limitations; the energy levels are not well defined, the wavefunctions are wavepackets superpositions and the elementary quasi-particle and collective excitations (with their finite lifetime) are relevant for the quantum-mechanical motion. In addition, in condensed matter we measure quantum-mechanical expectation values and statistical averages, a situation which bring us close to a quasi-classical approximation. Moreover, the rapid oscillations in space and time of the wave functions and the fields in condensed matter are locally averaged in a coarse-graining average, which enables a quasi-classical description. Let O_i be a dynamical variable of the i-th atomic constituent in a set of N such constituents placed around any point in a sample of condensed matter, and let $O = N^{-1}\sum_{i=1}^{N} O_i$ be the coarse-graining average. The motion of any O_i may imply a small amount of mechanical action, of the order of $\hbar$, but only large amounts of mechanical action are relevant, corresponding to the average O. Consequently, we may apply a quasi-classical approximation in these conditions. Moerover, we can see that even for small quantum numbers corresponding to the motion of any O_i this approximation is now valid. Such a quasi-classical approximation is described in this book for magnetic resonance and nuclear quadrupole resonance. In addition, by means of this method of quasi-classical description, a new feature, called parametric resonance, is revealed in the rotation spectra exhibited by molecules endowed with an electric dipole moment or a magnetic moment and placed in a static electric field or a static magnetic field, respectively.

In conclusion, we may say that a new method of quasi-classical approximation is presented in this book, for treating the interaction of quantum-mechanical motion with an external time-dependent interaction; the method, which is derived from Heisenberg's equation of motion, belongs to the class of quasi-classical approximations in Quantum Mechanics (correspondence principle, the JWKB approximation, $\hbar \to 0$ limit), and it may prove useful in various spectroscopies in condensed matter.

2 Introduction

The Maxwell equations in vacuum read

$$div\mathbf{E} = 4\pi\rho \ , \ div\mathbf{H} = 0 \ ,$$
$$curl\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t} \ , \ curl\mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c}\mathbf{j} \ , \tag{2.1}$$

where $\mathbf{E}$ and $\mathbf{H}$ are the (real) electric and magnetic field, respectively, ρ and $\mathbf{j}$ are the charge and current densities, respectively, and c is the speed of light in vacuum ($c = 3 \times 10^{10} cm/s$); the charge and the current are related by the continuity equation

$$\frac{\partial \rho}{\partial t} + div\mathbf{j} = 0 \tag{2.2}$$

(charge conservation); they originate in the elementary charges and currents associated with the atomic structure of matter. For a point charge q placed at $\mathbf{r}_0$ the density is $\rho = q\delta(\mathbf{r} - \mathbf{r}_0)$ and the current density is $\mathbf{j} = q\dot{\mathbf{r}}_0\delta(\mathbf{r} - \mathbf{r}_0)$ (convection current).

Equations (2.1) tell that ρ and $\mathbf{j}$ generate electromagnetic fields. Indeed, we introduce the scalar potential Φ and the vector potential $\mathbf{A}$ through $\mathbf{E} = -(1/c)\partial\mathbf{A}/\partial t - grad\Phi$ and $\mathbf{H} = curl\mathbf{A}$ and see immediately that two Maxwell equations are satisfied identically ($div\mathbf{H} = 0$ and $curl\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t}$), while the remaining two equations lead to the wave equations

$$\frac{1}{c^2}\frac{\partial^2 \Phi}{\partial t^2} - \Delta\Phi = 4\pi\rho \ , \ \frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2} - \Delta\mathbf{A} = \frac{4\pi}{c}\mathbf{j} \ , \tag{2.3}$$

providing the Lorenz gauge $div\mathbf{A} + (1/c)\partial\Phi/\partial t = 0$ is satisfied; under the gauge transformations $\mathbf{A} \to \mathbf{A} + grad\chi$, $\Phi \to \Phi - (1/c)\partial\chi/\partial t$ which preserve the fields, the Lorenz condition amounts to $(1/c^2)(\partial^2\chi/\partial t^2) - \Delta\chi = 0$. Particular solutions of the wave equations are given by

Kirchhoff's retarded potentials

$$\Phi(\mathbf{r},t)=\int d\mathbf{r}'\frac{\rho(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)}{\left|\mathbf{r}-\mathbf{r}'\right|}\ ,$$
$$\mathbf{A}(\mathbf{r},t)=\frac{1}{c}\int d\mathbf{r}'\frac{\mathbf{j}(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)}{\left|\mathbf{r}-\mathbf{r}'\right|}\ . \tag{2.4}$$

The general solution is obtained by adding the free fields which satisfy the homogeneous (source-free) equations (2.3). It is worth noting that the fields given by equations (2.4) propagate (and are extended), while the charge and current distributions are localized. The Lorenz gauge in equations (2.4) is ensured by the charge conservation (continuity equation).

Free fields are generated conventionally by charges and currents placed at infinity; in the regions of interest they satisfy the free Maxwell equations; they act with the Lorentz force

$$\mathbf{f}=\rho\mathbf{E}+\frac{1}{c}\mathbf{j}\times\mathbf{H} \tag{2.5}$$

upon charges and currents placed in the regions of interest; these fields are external fields for these charges and currents. Under the action of the Lorentz force the state of motion of the charges and currents is changed.

The field generated by a charge and a current localized at some point in space acts upon the charges and currents localized at other points in space; this amounts also to saying that the fields generated by a charge and current distribution act upon the distribution that created them; this can be called an internal field. Therefore, there is an interaction between charges and currents on one side and their corresponding fields on the other, incorporated in the Maxwell equations. Indeed, we get easily from equations (2.1)

$$\frac{1}{8\pi}\frac{\partial}{\partial t}\left(E^2+H^2\right)+\mathbf{jE}+\frac{c}{4\pi}div(\mathbf{E}\times\mathbf{H})=0\ , \tag{2.6}$$

which tells that the electromagnetic energy $(E^2+H^2)/8\pi$ plus the mechanical work $\mathbf{jE}$ done by the field upon charges per unit time plus the energy radiated through the surface by the Poynting vector $\mathbf{S}=\frac{c}{4\pi}(\mathbf{E}\times\mathbf{H})$ is zero: the total energy of the electromagnetic field and charges and currents is conserved. It is easy to see that a convection current is $\mathbf{j} = \rho\mathbf{v}$, which justifies the interpretation of the term $\mathbf{jE}$ as the work done by the Lorentz force $\mathbf{f}$ given by equation (2.5) per unit time (and per unit volume). Such an equation of conservation of the energy can be written either for the fields produced by the distributions ρ and $\mathbf{j}$ (particular solutions of the Maxwell equations, internal fields), or for external fields, or for the total fields which are the sum of internal and external fields. We can see that energy conservation implies quadratic quantities in fields, while the fields obey the superposition principle (Maxwell equations are linear in fields); the energy of two superposed fields is not the sum of the energies of the two fields, which amounts to say that the fields interact. Similarly, we get from Maxwell equations (2.1)

$$\begin{gathered}\rho\mathbf{E} + \tfrac{1}{c}\mathbf{j} \times \mathbf{H} + \tfrac{1}{4\pi c}\tfrac{\partial}{\partial t}(\mathbf{E} \times \mathbf{H}) + \\ + \tfrac{1}{4\pi}(\mathbf{E} \times curl\mathbf{E} + \mathbf{H} \times curl\mathbf{H} - \mathbf{E}div\mathbf{E} - \mathbf{H}div\mathbf{H}) = 0 \ ,\end{gathered} \tag{2.7}$$

which tells that the Lorentz force plus the reaction of the field (field momentum $(\mathbf{E} \times \mathbf{H})/4\pi c$) plus the stress force of the field is zero; the total momentum of the charges, currents and field is conserved, as for a closed system. The components of the last term in equation (2.7) can be written as $\partial_j \sigma_{ij}$, where

$$\sigma_{ij} = \frac{1}{8\pi}\delta_{ij}(E^2 + H^2) - \frac{1}{4\pi}(E_i E_j + H_i H_j) \tag{2.8}$$

is a stress tensor. It is worth noting that energy conservation given by equation (2.6) shows that the electromagnetic field, apart from acting upon charges and currents, has and carries energy. Similarly, the momentum conservation given by equation (2.8) suggests the existence of a medium, similar with an elastic medium, which sustains an electromagnetic field which carries momentum and produces a stress; this medium is suggestive of a luminiferous aether.

In matter, there appear internal electromagnetic fields, produced by the charges and currents of the atomic constituents. Some of these charges and currents are permanent, some other are induced by external fields. By analogy with Gauss's law $div\mathbf{E} = 4\pi\rho$, we admit the existence of an electric field $\mathbf{P}$, called polarization, which generates a "material" charge density $\rho_m = -div\mathbf{P}$, such that we write Gauss's law in matter as

$$div\mathbf{E} = 4\pi\rho - 4\pi div\mathbf{P} \ , \ div(\mathbf{E} + 4\pi\mathbf{P}) = 4\pi\rho \ ; \tag{2.9}$$

since matter is usually electrically neutral, it is easy to see that the polarization $\mathbf{P}$ is in fact a density of dipoles moments. A current density $\mathbf{j}_p = \partial\mathbf{P}/\partial t$ corresponds to the charge density $\rho_p = -div\mathbf{P}$, such that the continuity equation is satisfied; therefore, the Maxwell-Ampere equation $curl\mathbf{H} = \frac{1}{c}\frac{\partial\mathbf{E}}{\partial t} + \frac{\mathbf{4\pi}}{\mathbf{c}}\mathbf{j}$ will include the term $\frac{4\pi}{c}\frac{\partial\mathbf{P}}{\partial t}$; in addition, this equation suggests also the existence of another current density given by a magnetic field $\mathbf{M}$, called magnetization, through $curl\mathbf{M} = \frac{1}{c}\mathbf{j}_m^{'}$; the continuity equation admits such a current density, since $div \cdot curl = 0$. It follows that the Maxwell-Ampere equation in matter can be written as

$$curl\mathbf{H} = \frac{1}{c}\frac{\partial\mathbf{E}}{\partial t} + \frac{\mathbf{4\pi}}{\mathbf{c}}\mathbf{j} + \frac{4\pi}{c}\frac{\partial\mathbf{P}}{\partial t} + 4\pi curl\mathbf{M} \ ; \tag{2.10}$$

in matter, instead of $\mathbf{H}$, we denote this magnetic field by $\mathbf{B}$, and call it magnetic induction; the magnetic field is $\mathbf{H} = \mathbf{B} - 4\pi\mathbf{M}$. Introducing also the electric displacement $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$ we get the Maxwell equations in matter

$$\begin{gathered} div\mathbf{D} = 4\pi\rho \ , \ div\mathbf{B} = 0 \ , \\ curl\mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t} \ , \ curl\mathbf{H} = \frac{1}{c}\frac{\partial\mathbf{D}}{\partial t} + \frac{4\pi}{c}\mathbf{j} \ , \end{gathered} \tag{2.11}$$

where ρ and $\mathbf{j}$ are external charge and current densities, respectively. We have here two independent equations and four unknowns. Additional knowledge is necessary in order to solve these equations. It is easy to see that magnetization is the density of magnetic moments, similar with the polarization, which is the density of dipole moments. Indeed, the density of magnetic moments is $\frac{1}{2c}\mathbf{r} \times \mathbf{j}_m$ and the total magnetic moment is

$$\frac{1}{2c}\int d\mathbf{r} \cdot \mathbf{r} \times \mathbf{j}_m = \frac{1}{2}\int d\mathbf{r} \cdot \mathbf{r} \times curl\mathbf{M} = \int d\mathbf{r}\mathbf{M} \ . \tag{2.12}$$

In this respect, the "magnetic" current density is reminiscent of Ampere's molecular currents (or "electric vortices"). From equations

(2.11) we get the energy conservation

$$\frac{1}{4\pi}\left(\mathbf{E}\frac{\partial \mathbf{D}}{\partial t}+\mathbf{H}\frac{\partial \mathbf{B}}{\partial t}\right)+\mathbf{jE}+\frac{c}{4\pi}div(\mathbf{E}\times\mathbf{H})=0 \tag{2.13}$$

and the momentum conservation

$$\begin{gathered}\rho\mathbf{E}+\tfrac{1}{c}\mathbf{j}\times\mathbf{B}+\tfrac{1}{4\pi c}\tfrac{\partial}{\partial t}(\mathbf{D}\times\mathbf{B})+\\ +\tfrac{1}{4\pi}(\mathbf{D}\times curl\mathbf{E}+\mathbf{B}\times curl\mathbf{H}-\mathbf{E}div\mathbf{D}-\mathbf{H}div\mathbf{B})=0\ .\end{gathered} \tag{2.14}$$

3 Electric and Magnetic Moments

3.1 Electric dipole and quadrupole moments

With usual notations the scalar electromagnetic potential is given by Kirchhoff's solution

$$\Phi(\mathbf{r},t)=\int d\mathbf{r}'\frac{\rho(\mathbf{r}',t-\left|\mathbf{r}-\mathbf{r}'\right|/c)}{\left|\mathbf{r}-\mathbf{r}'\right|}\ \ , \tag{3.1}$$

where ρ is the charge density (and c denotes the speed of light); it is a particular solution of the wave equation

$$\frac{1}{c^2}\frac{\partial^2\Phi}{\partial t^2}-\Delta\Phi=4\pi\rho\ . \tag{3.2}$$

In matter charges perform a finite motion, so we can average equation (3.2) over this motion and get the static equation

$$\Delta\Phi=-4\pi\rho \tag{3.3}$$

and the Coulomb potential

$$\Phi(\mathbf{r})=\int d\mathbf{r}'\frac{\rho(\mathbf{r}')}{\left|\mathbf{r}-\mathbf{r}'\right|}\ ; \tag{3.4}$$

in this limit the electric field is given by

$$\mathbf{E}=-grad\Phi=\int d\mathbf{r}'\frac{\rho(\mathbf{r}-\mathbf{r}')}{\left|\mathbf{r}-\mathbf{r}'\right|^3}\ . \tag{3.5}$$

Similar results are obtained in the quasi-static limit, where the wavelengths are much larger than the relevant distances. For charges distributed over distances much smaller than the distance of observation r we may limit ourselves to $\rho(\mathbf{r}', t - r/c)/\left|\mathbf{r} - \mathbf{r}'\right|$ in equation (3.1); this quantity can be expanded in powers of $\mathbf{r}'$. For a classical charge q localized at $\mathbf{r}_0$ the charge density is $\rho(\mathbf{r}) = q\delta(\mathbf{r} - \mathbf{r}_0)$, and we have to expand the function $q/\left|\mathbf{r} - \mathbf{r}_0\right|$ in powers of $\mathbf{r}_0$. A quantum charge density is $\rho = q\left|\psi(\mathbf{r}, t)\right|^2$, where ψ is the wavefunction, and we need to expand the function $q\left|\psi(\mathbf{r}', t - r/c)\right|^2 / \left|\mathbf{r} - \mathbf{r}'\right|$ in powers of $\mathbf{r}'$; similarly, for several charges the charge density is given in terms of the multi-particle wavefunction (or the field operator for identical particles). Usually, the particle density $\left|\psi(\mathbf{r}, t)\right|^2$ is localized over a limited space region of some extension r_0, which amounts to an integration over this region of the expansion of the function $\left|\psi(\mathbf{r}', t - r/c)\right|^2 / \left|\mathbf{r} - \mathbf{r}'\right|$ in powers of $\mathbf{r}'$. We can see that the expansion in multipoles of the electromagnetic field is an expansion with generic coefficients (the multipoles), which are determined by the particular structure of the charge distribution. In this context it is worth recalling the quantum nature of the field equations like equation (3.2).

Let us consider a classical point charge q placed at $\mathbf{r}_0$; the potential becomes

$$\Phi = \frac{q}{\left|\mathbf{r} - \mathbf{r}_0\right|} = \frac{q}{r} + \frac{q\mathbf{r}_0\mathbf{r}}{r^3} + \frac{1}{2}qx_{0i}x_{0j}\frac{3x_ix_j - r^2\delta_{ij}}{r^5} + \dots \ , \tag{3.6}$$

where we have expanded in powers of x_{0i} ($r \gg r_0$) (and summation over repeated indices is included). We may also sum over several charges. The first term $\Phi_0 = q/r$ is the Coulomb law, the second term

$$\Phi_1 = \frac{q\mathbf{r}_0\mathbf{r}}{r^3} = \frac{\mathbf{d}\mathbf{r}}{r^3} \ , \ \mathbf{d} = q\mathbf{r}_0 \tag{3.7}$$

is the dipole contribution, the third term

$$\Phi_2 = \frac{1}{2}qx_{0i}x_{0j}\frac{3x_ix_j - r^2\delta_{ij}}{r^5} \tag{3.8}$$

is the quadrupole contribution; $\mathbf{d} = q\mathbf{r}_0$ is the dipole moment, its electric field is

$$\mathbf{E}_1 = -grad\frac{\mathbf{dr}}{r^3} = \frac{3(\mathbf{dr})\mathbf{r} - r^2\mathbf{d}}{r^5} \ . \tag{3.9}$$

Since

$$\Delta\frac{1}{r} = \delta_{ij}\frac{3x_i x_j - r^2\delta_{ij}}{r^5} = 0 \ , \tag{3.10}$$

we can write the quadrupole contribution as

$$\begin{aligned}\Phi_2 = \tfrac{1}{6}q(3x_{0i}x_{0j} - r_0^2\delta_{ij})\tfrac{3x_i x_j - r^2\delta_{ij}}{r^5} = \\ = \tfrac{1}{2}q(3x_{0i}x_{0j} - r_0^2\delta_{ij})\tfrac{x_i x_j}{r^5} = \tfrac{1}{2}D_{ij}\tfrac{x_i x_j}{r^5} \ ,\end{aligned} \tag{3.11}$$

where

$$D_{ij} = q(3x_{0i}x_{0j} - r_0^2\delta_{ij}) \tag{3.12}$$

is the quadrupole moment; it is a traceless tensor with five components. The quadrupole electric field is given by

$$E_{2i} = \frac{3}{2}D_{ij}\frac{x_j}{r^5} \ . \tag{3.13}$$

The quadrupole moment can be brought to its principal axes; since it is traceless, only two diagonal components are independent. If the charge distribution is symmetric about the z-axis, we have

$$D_{xx} = D_{yy} = -\frac{1}{2}D_{zz} \tag{3.14}$$

and

$$\Phi_2 = \frac{1}{4r^3}D(3\cos^2\theta - 1) = \frac{1}{2r^3}DP_2(\cos\theta) \ , \tag{3.15}$$

where θ is the angle between $\mathbf{r}$ and the z-axis, $D = D_{zz}$ and P_2 is the Legendre polynomial of the 2-nd order.

If the total charge is zero, the dipole moment does not depend on the origin of coordinates; if the total charge and the dipole moment are zero, the quadrupole moment does not depend on the origin of coordinates.

In general, we have the expansion

$$\frac{1}{|\mathbf{r}-\mathbf{r}_0|} = \sum_{l=0}^{\infty} \frac{r_0^l}{r^{l+1}} P_l(\cos\Theta) = \\ = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{r_0^l}{r^{l+1}} \frac{4\pi}{2l+1} Y_{lm}(\theta_0,\varphi_0) Y^*_{lm}(\theta,\varphi) \tag{3.16}$$

in spherical functions, which allows the representation

$$\Phi = \sum_{lm} \sqrt{\frac{4\pi}{2l+1}} \frac{1}{r^{l+1}} Q_{lm} Y^*_{lm}(\theta,\varphi) \ , \tag{3.17}$$

where

$$Q_{lm} = \sqrt{\frac{4\pi}{2l+1}} \sum_a q_a r_a^l Y_{lm}(\theta_a,\varphi_a) \tag{3.18}$$

is the electric moment of the 2^l-th order; it includes summation over all charges a. We have

$$Q_{00} = \sum_a q_a \ , \ Q_{10} = i \sum_a q_a r_a \cos\theta_a = i d_z \ , \\ Q_{1\pm1} = \mp\frac{i}{\sqrt{2}} \sum_a q_a r_a \sin\theta_a e^{\pm i\varphi_a} = \mp\frac{i}{\sqrt{2}}(d_x \pm i d_y) \tag{3.19}$$

and

$$Q_{20} = \frac{1}{2}\sum_a q_a r_a^2 (1 - 3\cos^2\theta_a) = -\frac{1}{2} D_{zz} \ , \\ Q_{2\pm1} = \pm\sqrt{\frac{3}{2}} \sum_a q_a r_a^2 \cos\theta_a \sin\theta_a e^{\pm i\varphi_a} = \\ = \pm\frac{1}{\sqrt{6}}(D_{xz} \pm i D_{yz}) \ , \\ Q_{2\pm2} = -\frac{1}{2}\sqrt{\frac{3}{2}} \sum_a q_a r_a^2 \sin^2\theta_a e^{\pm 2i\varphi_a} = \\ = -\frac{1}{2\sqrt{6}}(D_{xx} - D_{yy} \pm 2i D_{xy}) \ . \tag{3.20}$$

Let us assume that a charge distribution is placed in an external field with scalar potential Φ; the energy of the charge distribution in this external field is given by

$$U = \sum_a q_a \Phi(\mathbf{r}_a) \ . \tag{3.21}$$

We may expand $\Phi(\mathbf{r}_a)$ in powers of the coordinates x_{ai},

$$U = U_0 + U_1 + U_2 + \ , \tag{3.22}$$

where

$$U_0 = \Phi_0 \sum_a q_a \ , \tag{3.23}$$

$$U_1 = grad\Phi_0 \sum_a q_a \mathbf{r}_a = -\mathbf{d}\mathbf{E}_0 \tag{3.24}$$

and U_2 is the quadrupole contribution. The suffix 0 denotes the origin (around which the distribution is placed), $\mathbf{d}$ is the dipole moment and $\mathbf{E}_0$ is the electric field at the origin. Up to the first-order approximation the force acting upon the charge distribution is given by

$$\mathbf{F} = \mathbf{E}_0 \sum_a q_a + (\mathbf{d} grad)\ \mathbf{E}|_0 + ... \tag{3.25}$$

and the torque is given by

$$\mathbf{K} = \sum_a q_a \mathbf{r}_a \times \mathbf{E}_0 = \mathbf{d} \times \mathbf{E}_0 \ . \tag{3.26}$$

The rotation of a rigid dipole $d = ql$ under the action of the torque of forces given by equation (3.26) implies the motion of the angular momentum $L = mvl$, $d\mathbf{L}/dt = \mathbf{K} = \mathbf{d} \times \mathbf{E}_0$. If we leave aside the azimuthal motion, the equation of motion is $ml^2\ddot{\theta} = -qlE_0 \sin\theta$, where θ is the angle between $\mathbf{d}$ and $\mathbf{E}_0$; for small angles θ and a constant field, this is the equation of motion of a harmonic oscillator with frequency $\omega = \sqrt{qE_0/ml} = \sqrt{dE_0/I}$, where $I = ml^2$ is the moment of inertia; the quantum counterpart reads $I\omega^2 = \omega L = dE_0$ $(L = I\omega)$ and $\omega = dE/\hbar$, where $\hbar$ is Planck's constant; such a frequency is known as the Rabi frequency.[1]

The energy of a dipole in the field generated by another dipole is

$$U = -\mathbf{d}_1\mathbf{E}_2 = \frac{(\mathbf{d}_1\mathbf{d}_2)r^2 - 3(\mathbf{d}_1\mathbf{r})(\mathbf{d}_2\mathbf{r})}{r^5} \ , \tag{3.27}$$

[1] I. I. Rabi, "On the process of space quantization", Phys. Rev. **49** 324 (1936); I. I. Rabi, "Space quantization in a gyrating magnetic field", Phys. Rev. **51** 652 (1937).

where we have used the dipole field given by equation (3.9). Similarly, for a charge q in the field of a dipole we have the energy

$$U = q\frac{\mathbf{dr}}{r^3} \ . \tag{3.28}$$

The quadrupole contribution to the interaction energy is

$$U_2 = \tfrac{1}{2}\sum_a q_a x_{ai} x_{aj} \tfrac{\partial^2 \Phi_0}{\partial x_i \partial x_j} = \tfrac{1}{2}\sum_a q_a (x_{ai} x_{aj} - \tfrac{1}{3}\delta_{ij} r_a^2) \tfrac{\partial^2 \Phi_0}{\partial x_i \partial x_j} =$$
$$= \tfrac{1}{6} D_{ij} \tfrac{\partial^2 \Phi_0}{\partial x_i \partial x_j} \ . \tag{3.29}$$

In general, since

$$\Phi(\mathbf{r}_a) = \sum_{lm} r^l \sqrt{\frac{4\pi}{2l+1}} a_{lm} Y_{lm}(\theta_a, \varphi_a) \tag{3.30}$$

we get

$$U = \sum_a q_a \Phi(\mathbf{r}_a) = \sum_{lm} a_{lm} Q_{lm} \ \ , \tag{3.31}$$

where Q_{lm} is the moment given by equation (3.18) and a_{lm} are the coefficients of the expansion of the potential in spherical harmonics.

3.2 Magnetic Moments

With usual notations the vector potential is given by Kirchhoff's solution

$$\mathbf{A}(\mathbf{r}, t) = \frac{1}{c}\int d\mathbf{r}' \frac{\mathbf{j}(\mathbf{r}', t - |\mathbf{r} - \mathbf{r}'| / c)}{|\mathbf{r} - \mathbf{r}'|} \ \ , \tag{3.32}$$

where $\mathbf{j}$ is the curent density (and c denotes the speed of light); it is a particular solution of the wave equation

$$\frac{1}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2} - \Delta \mathbf{A} = \frac{4\pi}{c}\mathbf{j} \ . \tag{3.33}$$

In the quasi-static limit it becomes

$$\Delta \mathbf{A} = -\frac{4\pi}{c}\mathbf{j} \ , \tag{3.34}$$

hence

$$\mathbf{A}(\mathbf{r},t) \simeq \frac{1}{c}\int d\mathbf{r}' \frac{\mathbf{j}(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} \ ; \tag{3.35}$$

this is the Biot-Savart law for the magnetic field

$$\mathbf{H} = curl\mathbf{A} = \frac{1}{c}\int d\mathbf{r}' \frac{\mathbf{j}\times(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} \ . \tag{3.36}$$

If we take the average of equation (3.33) over finite motion of charges in matter we get the static equation $\Delta\overline{\mathbf{A}} = 0$, since $\overline{\mathbf{j}} = 0$. It is worth noting that the quasi-static potentials Φ and $\mathbf{A}$ satisfy the Lorenz gauge $div\mathbf{A} + (1/c)\partial\Phi/\partial t = 0$ (due to the the continuity equation $\partial\rho/\partial t + div\mathbf{j} = 0$).

According to equation (3.35), the quasi-static vector potential $\mathbf{A}$ generated by a point charge q_a moving at $\mathbf{r}_a$ with velocity $\mathbf{v}_a$ *(i.e.* a current density $\mathbf{j}_a = q\mathbf{v}_a\delta(\mathbf{r}-\mathbf{r}_a)$) is given by

$$\mathbf{A}(\mathbf{r},t) = \frac{1}{c}q_a\frac{\mathbf{v}_a}{|\mathbf{r}-\mathbf{r}_a|} \ ; \tag{3.37}$$

far away from the charge we have the expansion

$$\mathbf{A} = \frac{1}{c}q_a\frac{\mathbf{v}_a}{r} + \frac{1}{c}q_a\frac{\mathbf{v}_a(\mathbf{r}_a\mathbf{r})}{r^3} + ..., \tag{3.38}$$

where we can write

$$\mathbf{v}_a(\mathbf{r}_a\mathbf{r}) = \frac{1}{2}\frac{d}{dt}[\mathbf{r}_a(\mathbf{r}_a\mathbf{r})] + \frac{1}{2}[\mathbf{v}_a(\mathbf{r}_a\mathbf{r}) - \mathbf{r}_a(\mathbf{v}_a\mathbf{r})] \ ; \tag{3.39}$$

the classical Electromagnetism admits that the macroscopic fields arise from macroscopic charges and currents, *i.e.* from microscopic charges and currents averaged over their finite motion in matter; consequently, we have $\overline{\mathbf{v}}_a = 0$ and

$$\overline{\mathbf{v}_a(\mathbf{r}_a\mathbf{r})} = \frac{1}{2}\overline{[\mathbf{v}_a(\mathbf{r}_a\mathbf{r}) - \mathbf{r}_a(\mathbf{v}_a\mathbf{r})]} = \frac{1}{2}\overline{(\mathbf{r}_a\times\mathbf{v}_a)}\times\mathbf{r} \ , \tag{3.40}$$

i.e.

$$\overline{\mathbf{A}} = \frac{1}{2c}q_a\frac{\overline{(\mathbf{r}_a\times\mathbf{v}_a)}\times\mathbf{r}}{r^3} = \frac{\overline{\mathbf{m}}\times\mathbf{r}}{r^3} \ , \tag{3.41}$$

where

$$\overline{\mathbf{m}} = \frac{1}{2c} q_a \overline{\mathbf{r}_a \times \mathbf{v}_a} \tag{3.42}$$

is the magnetic momentum of the charge q_a; we can sum over all charges (and can even admit a continuous charge and current distribution). From equation (3.41) we get easily the magnetic field

$$\overline{\mathbf{H}} = curl\overline{\mathbf{A}} = \frac{3(\overline{\mathbf{m}}\mathbf{r})\mathbf{r} - \overline{\mathbf{m}}r^2}{r^5} \tag{3.43}$$

(by using $\varepsilon_{ijk}\varepsilon_{ilm} = \delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}$), which indicates that the magnetic moment acts as a magnetic dipole. If the ratio charge-to-mass is the same for all particles (q/m) we can write

$$\overline{\mathbf{m}} = \frac{q}{2mc}\sum_a m_a \overline{\mathbf{r}_a \times \mathbf{v}_a} = \frac{q}{2mc}\mathbf{L} \ , \tag{3.44}$$

where $\mathbf{L}$ is the (mechanical) angular momentum. Since $(1/2)\mathbf{r} \times \mathbf{v} = \Delta S/\Delta t$, where ΔS is the area covered by a macroscopic rotation in time Δt, we get from equation (3.42) $m = I\Delta S/c$ for the magnetic moment of a macroscopic current $I = q/\Delta t$ (a coil). Indeed, the magnetic moment $m = IS/c = q\nu\pi r^2/c = q\omega r^2/2c$ of a charge q moving in a circular orbit (radius r, area $S = \pi r^2$, frequency $\nu = \omega/2\pi$, current $I = q\nu$) is related to the angular momentum $L = mvr = m\omega r^2$ through $m = (q/2mc)L$ (where m is the mass of the particle).

It is worth noting that a statistical average of the orbital currents or magnetic moments with classical statistics gives vanishing currents and magnetic moments, a result which is known as Bohr-van Leuween theorem (it is due to the kinetic energy in the classical statistical distribution, which is quadratic in velocities); classically, there is no magnetic moment (and no magnetism).[2] The quantum average of orbital currents (momenta) over bound states in centrally symmetric fields is also vanishing, due to the conservation of parity; in general, the (averaged) orbital currents in matter are "quenched", *i.e.* they are vanishing.

[2] N. Bohr, Disertation, Copenhagen (1911); J. H. van Leeuwen, Disertation, Leiden (1919); J. H. van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford (1932).

The force acting upon an assembly of moving charges placed in a constant magnetic field $\mathbf{H}$ is zero:

$$\mathbf{F} = \sum_a \frac{q_a}{c} \overline{\mathbf{v}_a \times \mathbf{H}} = \sum_a \frac{q_a}{c} \overline{\frac{d}{dt}(\mathbf{r}_a \times \mathbf{H})} = 0 \ ; \tag{3.45}$$

the torque is given by

$$\begin{aligned} \mathbf{K} = \textstyle\sum_a \frac{q_a}{c} \overline{\mathbf{r}_a \times (\mathbf{v}_a \times \mathbf{H})} = \sum_a \frac{q_a}{c} \overline{\mathbf{v}_a (\mathbf{r}_a \mathbf{H}) - \frac{1}{2}\mathbf{H} \frac{d}{dt}(r_a^2)} = \\ = \textstyle\sum_a \frac{q_a}{c} \overline{\mathbf{v}_a (\mathbf{r}_a \mathbf{H})} \ , \end{aligned} \tag{3.46}$$

or

$$\begin{aligned} \mathbf{K} = \textstyle\sum_a \frac{q_a}{2c} \overline{\mathbf{v}_a (\mathbf{r}_a \mathbf{H}) - \mathbf{r}_a (\mathbf{v}_a \mathbf{H})} = \\ = \textstyle\sum_a \frac{q_a}{2c} \mathbf{H} \times \overline{(\mathbf{v}_a \times \mathbf{r}_a)} = \overline{\mathbf{m}} \times \mathbf{H} \end{aligned} \tag{3.47}$$

(by using the same averaging procedure as given above for the magnetic moment); we can compare this magnetic torque with the electric torque acting upon a dipole as given by equation (3.26).

The lagrangian of the charges in a uniform magnetic field $\mathbf{H}$ with the vector potential $\mathbf{A} = (\mathbf{H} \times \mathbf{r})/2$ includes the additional term

$$L_H = \sum_a \frac{q_a}{c} \mathbf{A} \mathbf{v}_a = \sum_a \frac{q_a}{2c} (\mathbf{H} \times \mathbf{r}) \mathbf{v}_a \ , \tag{3.48}$$

which, on averaging, leads to

$$L_H = \overline{\mathbf{m}} \mathbf{H} \ ; \tag{3.49}$$

the corresponding energy is

$$E_H = -\overline{\mathbf{m}} \mathbf{H} \ ; \tag{3.50}$$

it is similar with the dipole energy ($E_E = -\mathbf{d}\mathbf{E}$) in an electric field, as given by equation (3.24).

Let us assume an assembly of charges with the lagrangian

$$L = \sum_a \frac{1}{2} m_a v_a^2 - U \tag{3.51}$$

with usual notations, where U is their potential energy (including a centrally symmetric field and interaction). In a frame rotating with angular velocity $\overrightarrow{\Omega}$ the velocity is given by

$$\mathbf{v} = \mathbf{v}^{'} + \overrightarrow{\Omega} \times \mathbf{r}^{'} \ , \tag{3.52}$$

while the potential energy does not change. The lagrangian becomes

$$L = \sum_a [\frac{1}{2} m_a v_a^{'2} + m_a \overrightarrow{\Omega} (\mathbf{r}_a^{'} \times \mathbf{v}_a^{'}) + \frac{1}{2} m_a (\overrightarrow{\Omega} \times \mathbf{r}_a^{'})^2] - U \ ; \tag{3.53}$$

for the same ratio charge-to-mass (q/m) and for $\overrightarrow{\Omega} = \frac{q}{2mc}\mathbf{H}$ we can see that the lagrangian acquires a magnetic term $\overline{\mathbf{m}}\mathbf{H}$ (on averaging over the finite microscopic motion of charges), providing the magnetic field $\mathbf{H}$ (and angular velocity $\overrightarrow{\Omega}$) are sufficiently small as to neglect the quadratic term in H^2 (Ω^2). This is known as Larmor's theorem; the angular velocity $\Omega = |q| \, H/2mc$ is called the Larmor frequency.

The torque given by equation (3.47) moves the angular momentum,

$$\frac{d\mathbf{L}}{dt} = \mathbf{K} = \overline{\mathbf{m}} \times \mathbf{H} \ ; \tag{3.54}$$

using equation (3.44) (for the same ratio charge-to-mass) we get

$$\frac{d\overline{\mathbf{m}}}{dt} = \frac{q}{2mc} \overline{\mathbf{m}} \times \mathbf{H} \tag{3.55}$$

and

$$\frac{d\mathbf{L}}{dt} = \frac{q}{2mc} \mathbf{L} \times \mathbf{H} = -\overrightarrow{\Omega} \times \mathbf{L} \ . \tag{3.56}$$

Equation (3.55) is known as Larmor's equation of motion (precession); $\gamma = q/2mc$ is called the gyromagnetic ratio (factor).

It is worth noting that the motion of a charge q in a constant magnetic field H proceeds according to the equations $m\dot{v}_x = \frac{q}{c} v_y H$, $m\dot{v}_y = -\frac{q}{c} v_x H$, *i.e.* $\ddot{v}_x = (qH/mc)^2 v_x$; this motion oscillates with the frequency $\frac{qH}{mc}$, which is known as the cyclotron frequency. It is the average over microscopic motion which makes the magnetic moment and the angular momentum to precess with Larmor's frequency $\frac{qH}{2mc}$. Quasi-classical motion in matter in the presence of a magnetic field proceeds with cyclotron frequency.