or in the interaction representation

$$V_{\rm I} = -\sum_a y_a{}^{\rm I} f_a(t). \qquad (14.6\text{-}48)$$

We may wish to know the response associated with the change in expectation value of one of the operators $y^{\rm I}$, say $y_b{}^{\rm I}$. From (14.6-44) it follows that

$$\Delta\langle y_b{}^{\rm I}\rangle = \sum_a \int_{-\infty}^{\infty} K_{ba}(\tau) f_a(t-\tau)\, d\tau \qquad (14.6\text{-}49)$$

where

$$K_{ba}(\tau) = \frac{i}{\hbar}\langle[y_b{}^{\rm I}(t), y_a{}^{\rm I}(t-\tau)]\rangle \qquad (14.6\text{-}50)$$

or in terms of a density operator

$$K_{ba}(\tau) = \frac{i}{\hbar}\mathrm{Tr}\{[y_b{}^{\rm I}(t), y_a{}^{\rm I}(t-\tau)]\rho\}. \qquad (14.6\text{-}51)$$

Similarly the susceptibility is

$$\chi_{ba}(\omega) = \int_{-\infty}^{\infty} K_{ba}(\tau) e^{i\omega\tau}\, d\tau$$
$$= \frac{i}{\hbar}\int_{-\infty}^{\infty} \mathrm{Tr}\{[y_b{}^{\rm I}(t), y_a{}^{\rm I}(t-\tau)]\rho\} e^{i\omega\tau}\, d\tau. \qquad (14.6\text{-}52)$$

An application to optical susceptibility is discussed in Section 24.4.

CHAPTER 15

DIRAC EQUATION

The phenomena occurring in atoms and molecules are describable, for the most part, on the basis of nonrelativistic quantum mechanics. It is nevertheless advantageous to start with the relativistic equation of Dirac and to proceed to its nonrelativistic approximation. In doing so one obtains expressions for the various interaction terms that appear in the Schrödinger Hamiltonian and no further derivations are required. Strictly speaking, this approach is rigorous only for the one-electron case because the Dirac equation applies only to a single particle. Still, much of the information obtained by this route is also applicable to a many-electron system.

The Dirac equation for a free particle serves to introduce the formalism. Electromagnetic couplings are then added and the approximation to order v^2/c^2 provides the desired results.

15.1 Free Particle Equation

The time-independent Dirac equation for a free particle is

$$(c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2)\psi = E\psi \qquad (15.1\text{-}1)$$

in which

$$\alpha_x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \qquad \alpha_y = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}, \qquad (15.1\text{-}2)$$

and, substituting in (15.1-16),

$$E'\psi_u = \frac{p^2}{2m}\psi_u \tag{15.1-19}$$

or

$$E'\psi_u = -\frac{\hbar^2}{2m}\nabla^2\psi_u. \tag{15.1-20}$$

Equation (15.1-20) is still in two-component form since ψ_u is a two-component function. But each component of ψ_u satisfies (15.1-20) so that we may drop all subscripts and write

$$E'\psi = -\frac{\hbar^2}{2m}\nabla^2\psi \tag{15.1-21}$$

which is the time-independent Schrödinger equation for a free particle.

15.2 Dirac Equation with Electromagnetic Coupling

The free-particle Dirac equation (15.1-1) must now be modified to include effects due to external fields. Classical considerations suggest how this may be accomplished. In the presence of external fields a possible Lagrangian for the system is

$$L = \frac{1}{2}mv^2 + \frac{q}{c}\mathbf{v}\cdot\mathbf{A} - q\varphi \tag{15.2-1}$$

in which v is the velocity of a particle with positive charge q and mass m, $\mathbf{A}$ and φ are the vector and scalar potentials, respectively. The fields are then given by

$$\mathbf{B} = \nabla\times\mathbf{A}, \qquad \mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t} - \nabla\varphi. \tag{15.2-2}$$

To verify that a Lagrangian of form (15.2-1) leads to correct physical results it is sufficient to demonstrate the derivation of the Lorentz force law

$$\mathbf{F} = q\left(\mathbf{E} + \frac{1}{c}\mathbf{v}\times\mathbf{B}\right) \tag{15.2-3}$$

from (15.2-1). Thus the Lagrange equations

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}_i}\right) = \frac{\partial L}{\partial x_i} \qquad (x_i = x, y, z), \tag{15.2-4}$$

with the Lagrangian as in (15.2-1), become

$$\frac{\partial L}{\partial x_i} = m\ddot{x}_i + \frac{q}{c}\frac{dA_i}{dt} \tag{15.2-5}$$

where, for example,

$$\frac{dA_x}{dt} = \frac{\partial A_x}{\partial x}\dot{x} + \frac{\partial A_x}{\partial y}\dot{y} + \frac{\partial A_x}{\partial z}\dot{z} + \frac{\partial A_x}{\partial t} \tag{15.2-6}$$

is the total time derivative of A_x and the last term on the right represents the intrinsic time dependence, if any, of A_x. Since

$$\frac{\partial L}{\partial x} = \frac{q}{c}\left(\frac{\partial A_x}{\partial x}\dot{x} + \frac{\partial A_y}{\partial x}\dot{y} + \frac{\partial A_z}{\partial x}\dot{z}\right) - q\frac{\partial\varphi}{\partial x}$$

the Lagrange equation (15.2-5) for the x component is

$$\begin{aligned} m\ddot{x} &= q\left[\frac{1}{c}\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right)\dot{y} - \frac{1}{c}\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right)\dot{z} - \frac{1}{c}\frac{\partial A_x}{\partial t} - \frac{\partial\varphi}{\partial x}\right] \\ &= q\left[E_x + \frac{1}{c}(\mathbf{v}\times\mathbf{B})_x\right] = F_x. \end{aligned} \tag{15.2-7}$$

The other components are obtained in similar fashion thus verifying the derivation of the Lorentz force law from (15.2-1).

On this basis one may now proceed to define the canonical momentum

$$p_i = \frac{\partial L}{\partial \dot{x}_i} = m\dot{x}_i + \frac{q}{c}A_i \tag{15.2-8}$$

and the Hamiltonian

$$\mathscr{H} = \sum_i \frac{\partial L}{\partial \dot{x}_i}\dot{x}_i - L = \mathbf{p}\cdot\mathbf{v} - L = \frac{1}{2m}\left(\mathbf{p} - \frac{q}{c}\mathbf{A}\right)^2 + q\varphi. \tag{15.2-9}$$

Equations (15.2-8) and (15.2-9) indicate the modifications in the canonical momenta and the Hamiltonian brought about by the presence of the external fields.

It will now be assumed that the same modifications can be introduced into the free particle Dirac equation (15.1-1) so that the proper equation for a particle of (positive) charge q and rest mass m in a field with vector potential $\mathbf{A}$ and scalar potential φ is

$$[\boldsymbol{\alpha}\cdot(c\mathbf{p} - q\mathbf{A}) + \beta mc^2 + q\varphi]\psi = E\psi. \tag{15.2-10}$$

Needless to say this classical development is merely suggestive; the Dirac equation is to be regarded as a fundamental equation whose validity must be investigated—ultimately by resort to experiment—independently of any classical arguments. In two-component form, by analogy with (15.1-9),

$$\boldsymbol{\sigma}\cdot(c\mathbf{p} - q\mathbf{A})\psi_v + (mc^2 + q\varphi)\psi_u = E\psi_u, \tag{15.2-11a}$$

$$\boldsymbol{\sigma}\cdot(c\mathbf{p} - q\mathbf{A})\psi_u - (mc^2 - q\varphi)\psi_v = E\psi_v. \tag{15.2-11b}$$

Therefore

$$\begin{aligned}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2(E'-q\varphi)+(E'-q\varphi)(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2 &\equiv (\boldsymbol{\sigma}\cdot\boldsymbol{\pi})[(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})(E'-q\varphi)-(E'-q\varphi)(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})]\\ &\quad-[(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})(E'-q\varphi)-(E'-q\varphi)(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})](\boldsymbol{\sigma}\cdot\boldsymbol{\pi})\\ &\quad+2(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})(E'-q\varphi)(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})\\ &= q\hbar^2\nabla\cdot\nabla\varphi-2q\hbar\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\times\nabla\varphi\\ &\quad+2(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})(E'-q\varphi)(\boldsymbol{\sigma}\cdot\boldsymbol{\pi}).\end{aligned} \tag{15.2-27}$$

Substitution of (15.2-27) into (15.2-24) gives

$$\begin{aligned}(E'-q\varphi)\psi=\Bigg[&\frac{1}{2m}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2-\frac{1}{8m^3c^2}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^4\\ &+\frac{q\hbar^2}{8m^2c^2}\nabla\cdot\nabla\varphi-\frac{q\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot\boldsymbol{\pi}\times\nabla\varphi\Bigg]\psi.\end{aligned} \tag{15.2-28}$$

Also, from (15.2-16),

$$\frac{1}{2m}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^2=\frac{1}{2m}\left(\mathbf{p}-\frac{q}{c}\mathbf{A}\right)^2-\frac{q\hbar}{2mc}\boldsymbol{\sigma}\cdot\nabla\times\mathbf{A} \tag{15.2-29}$$

and, to order v^2/c^2,

$$\frac{1}{c^2}(\boldsymbol{\sigma}\cdot\boldsymbol{\pi})^4=\frac{p^4}{c^2}, \tag{15.2-30}$$

$$\begin{aligned}\frac{1}{c^2}\boldsymbol{\pi}\times\nabla\varphi=\frac{1}{c^2}\mathbf{p}\times\nabla\varphi&=\frac{1}{c^2}(-i\hbar\nabla\times\nabla\varphi-\nabla\varphi\times\mathbf{p}).\\ &=-\frac{1}{c^2}\nabla\varphi\times\mathbf{p}.\end{aligned} \tag{15.2-31}$$

We shall now replace q by $-e$, where e is the magnitude (absolute value) of the electronic charge, to obtain the Dirac equation for an electron to order v^2/c^2:

$$\begin{aligned}(E'+e\varphi)\psi=\Bigg[&\frac{1}{2m}\left(\mathbf{p}+\frac{e}{c}\mathbf{A}\right)^2+\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\nabla\times\mathbf{A}\\ &-\frac{p^4}{8m^3c^2}-\frac{e\hbar^2}{8m^2c^2}\nabla\cdot\nabla\varphi-\frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot\nabla\varphi\times\mathbf{p}\Bigg]\psi.\end{aligned} \tag{15.2-32}$$

Equation (15.2-32), which may also be regarded as the Schrödinger equation for an electron interacting with fields describable by the potentials $\mathbf{A}$ and φ, is the starting point for discussions of atomic and molecular properties. The

significance of the various terms and their energies, indicated to within an order of magnitude, are:

$e\varphi$ scalar potential energy ($10^5\ \mathrm{cm}^{-1}$).

$(1/2m)(\mathbf{p}+(e/c)\mathbf{A})^2$ contains kinetic energy and interaction terms with a field represented by a vector potential $\mathbf{A}$ ($10^5\ \mathrm{cm}^{-1}$). The interaction terms are responsible or contribute to numerous physical processes among which are absorption, emission and scattering of electromagnetic waves, diamagnetism, and the Zeeman effect.

$(e\hbar/2mc)\boldsymbol{\sigma}\cdot\nabla\times\mathbf{A}$ interaction of the spin magnetic moment with a magnetic field $\mathbf{B}=\nabla\times\mathbf{A}$ ($1\ \mathrm{cm}^{-1}$).

$p^4/8m^3c^2$ this term appears in the expansion of the relativistic energy

$$\sqrt{(mc^2)^2+p^2c^2}=mc^2+\frac{p^2}{2m}-\frac{p^4}{8m^3c^2}+\cdots.$$

It is therefore a relativistic correction to the kinetic energy ($0.1\ \mathrm{cm}^{-1}$).

$-(e\hbar^2/8m^2c^2)\nabla\cdot\nabla\varphi$ produces an energy shift in s-states and is known as the Darwin term ($<0.1\ \mathrm{cm}^{-1}$).

$-(e\hbar/4m^2c^2)\boldsymbol{\sigma}\cdot\nabla\varphi\times\mathbf{p}$ spin-orbit interaction (10–$10^3\ \mathrm{cm}^{-1}$).

It is necessary to add a word of caution concerning the validity of (15.2-32) which contains the approximation

$$K=\frac{2mc^2}{E'+2mc^2-q\varphi}\approx 1-\frac{E'-q\varphi}{2mc^2}.$$

Clearly, this will not be legitimate if φ becomes singular as it does, for example, in certain hyperfine interactions. In such cases a separate treatment is required (see Section 18.1).