

Quantum Mechanics of a Charged Particle in an Electromagnetic Field

These notes present the Schrodinger equation for a charged particle in an external electromagnetic field. In order to obtain the relevant equation, we first examine the classical Hamiltonian of a charged particle in an electromagnetic field. We then use this result to obtain the Schrodinger equation using the principle of minimal substitution. We examine a special case of a uniform magnetic field. Finally, we demonstrate the origin of the coupling of the spin operator to the external magnetic field in the case of a charged spin-1/2 particle.

Note that in these notes, we assume that all motion is non-relativistic. Thus, we shall set $\gamma = (1 - v^2/c^2)^{-1/2} \simeq 1$.

I. Classical Hamiltonian of a charged particle in an electromagnetic field

We begin by examining the classical theory of a charged spinless particle in and external electric field \vec{E} and magnetic field \vec{B} . Gaussian (or cgs) units are employed for electromagnetic quantities. It is convenient to introduce the vector potential \vec{A} and the scalar potential ϕ :

$$\vec{B} = \vec{\nabla} \times \vec{A}, \quad \vec{E} = -\vec{\nabla} \phi - \frac{1}{c} \frac{\partial \vec{A}}{\partial t}. \quad (1)$$

These equations encode two of the four Maxwell equations,

$$\vec{\nabla} \cdot \vec{B} = 0, \quad \vec{\nabla} \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{B}}{\partial t}, \quad (2)$$

due to the vector identities

$$\vec{\nabla} \cdot (\vec{\nabla} \times \vec{A}) = 0, \quad \vec{\nabla} \times (\vec{\nabla} \phi) = 0,$$

which are valid for any non-singular vector field $\vec{A}(\vec{x}, t)$ and scalar field $\phi(\vec{x}, t)$.

However, the fields \vec{A} and ϕ are not unique. Namely, the following transformations:

$$\vec{A} \longrightarrow \vec{A} + \vec{\nabla} \chi(\vec{x}, t), \quad \phi \longrightarrow \phi - \frac{1}{c} \frac{\partial \chi(\vec{x}, t)}{\partial t}, \quad (3)$$

called *gauge transformations* leave the physical electromagnetic fields, \vec{E} and \vec{B} , unchanged.

We wish to write down a classical Hamiltonian H that describes the motion of a charged particle q in an external electromagnetic field. Given H , we can use Hamilton's equations to derive the equations of motion for the charged particle. The correct Hamiltonian will yield the Lorentz force law:

$$\vec{F} = \frac{d}{dt}(m\vec{v}) = q \left(\vec{E} + \frac{\vec{v}}{c} \times \vec{B} \right). \quad (4)$$

The Hamiltonian for a charged particle in an electromagnetic field is given by:

$$\boxed{H = \frac{1}{2m} \left(\vec{p} - \frac{q\vec{A}}{c} \right) \cdot \left(\vec{p} - \frac{q\vec{A}}{c} \right) + q\phi.} \quad (5)$$

We shall verify this result by using Hamilton's equations to compute the equations of motion and demonstrate that these coincide with eq. (4). For a Hamiltonian of the form $H = H(p_i, x_i)$, Hamilton's equations are given by:

$$\frac{\partial H}{\partial p_i} = \frac{dx_i}{dt}, \quad -\frac{\partial H}{\partial x_i} = \frac{dp_i}{dt},$$

where i runs over the three directions of space. In particular, the partial derivative with respect to p_i is computed at fixed x_i and the partial derivative with respect to x_i is computed at fixed p_i . Inserting eq. (5) into Hamilton's equations yields:

$$v_i \equiv \frac{dx_i}{dt} = \frac{p_i}{m} - \frac{q}{mc} A_i, \quad (6)$$

$$F_i \equiv \frac{dp_i}{dt} = \frac{q}{mc} \left(\vec{p} - \frac{q\vec{A}}{c} \right) \cdot \frac{\partial \vec{A}}{\partial x_i} - q \frac{\partial \phi}{\partial x_i}. \quad (7)$$

Eq. (6) is equivalent to:

$$\boxed{\vec{p} = m\vec{v} + \frac{q}{c}\vec{A}.}$$

The quantity $m\vec{v}$ is called the *mechanical momentum*, which is *not* equal to \vec{p} , which is called the *canonical momentum*. The reason for this nomenclature will be addressed later. If we now substitute the equation for \vec{p} in eq. (7), we obtain:

$$\frac{d}{dt} \left(mv_i + \frac{q}{c} A_i \right) = \frac{q}{c} \vec{v} \cdot \frac{\partial \vec{A}}{\partial x_i} - q \frac{\partial \phi}{\partial x_i}. \quad (8)$$

which we can rewrite as:

$$\frac{d}{dt}(mv_i) = \frac{q}{c} \left[\vec{v} \cdot \frac{\partial \vec{A}}{\partial x_i} - \frac{dA_i}{dt} \right] - q \frac{\partial \phi}{\partial x_i}. \quad (9)$$

To make further progress, note that $d\vec{A}/dt$ is a *full* time-derivative of \vec{A} . By the chain rule,

$$\frac{d\vec{A}}{dt} = \frac{\partial \vec{A}}{\partial t} + \sum_{j=1}^3 \frac{\partial \vec{A}}{\partial x_j} \frac{dx_j}{dt}.$$

The chain rule reflects the physical fact that the full time-derivative of \vec{A} has two sources: (i) explicit time-dependence of $\vec{A}(\vec{x}, t)$, and (ii) implicit time-dependence by virtue of the fact that the charged particle moves on a trajectory $\vec{x} = \vec{x}(t)$. Noting that $v_i \equiv dx_i/dt$ [where $\vec{x} \equiv (x_1, x_2, x_3)$], we can rewrite the chain rule above as:

$$\frac{dA_i}{dt} = \frac{\partial A_i}{\partial t} + (\vec{v} \cdot \vec{\nabla}) A_i.$$

Inserting this result in eq. (9) yields:

$$\frac{d}{dt}(mv_i) = \frac{q}{c} \left[\vec{v} \cdot \frac{\partial \vec{A}}{\partial x_i} - \frac{\partial A_i}{\partial t} - (\vec{v} \cdot \vec{\nabla}) A_i \right] - q \frac{\partial \phi}{\partial x_i}. \quad (10)$$

Next, we make use of the vector identity:

$$[\vec{v} \times (\vec{\nabla} \times \vec{A})]_i = \vec{v} \cdot \frac{\partial \vec{A}}{\partial x_i} - (\vec{v} \cdot \vec{\nabla}) A_i. \quad (11)$$

This should remind you of the BAC–CAB rule used for computing the triple cross-product: $\vec{A} \times (\vec{B} \times \vec{C}) = \vec{B}(\vec{A} \cdot \vec{C}) - \vec{C}(\vec{A} \cdot \vec{B})$. In the case of the identity above, you have to be careful since one of the vectors is a differential operator, which does not commute with \vec{x} . However, it is straightforward to prove eq. (11) by employing a well-known identity involving the product of two Levi Civita tensors:

$$[\vec{v} \times (\vec{\nabla} \times \vec{A})]_i = \epsilon_{ijk} v_j \epsilon_{klm} \frac{\partial A_m}{\partial x_\ell} = (\delta_{il} \delta_{jm} - \delta_{im} \delta_{jl}) v_j \frac{\partial A_m}{\partial x_\ell} = \vec{v} \cdot \frac{\partial \vec{A}}{\partial x_i} - (\vec{v} \cdot \vec{\nabla}) A_i, \quad (12)$$

where there is an implied sum over pairs of repeated indices. In light of eq. (11), one can rewrite eq. (10) as follows:

$$\frac{d}{dt}(m\vec{v}) = \frac{q}{c} \vec{v} \times (\vec{\nabla} \times \vec{A}) - q \left(\vec{\nabla} \phi + \frac{1}{c} \frac{\partial \vec{A}}{\partial t} \right).$$

Finally, using eq. (1), we end up with

$$\frac{d}{dt}(m\vec{v}) = q\vec{E} + \frac{q}{c} \vec{v} \times \vec{B},$$

which coincides with eq. (4), as required.

So far, we have described the motion of a charged particle in an external electromagnetic field. If the particle also feels an external potential $V(\vec{x}, t)$ that is unrelated to the external electromagnetic field, then we should use the more general Hamiltonian,

$$H = \frac{1}{2m} \left(\vec{p} - \frac{q\vec{A}}{c} \right) \cdot \left(\vec{p} - \frac{q\vec{A}}{c} \right) + q\phi + V(\vec{x}, t). \quad (13)$$

Eq. (13) suggests *the principle of minimal substitution*, which states that the Hamiltonian for a charged particle (of charge q) in an external electromagnetic field can be obtained from the corresponding Hamiltonian for an uncharged particle by making the following substitutions:

$$\vec{p} \longrightarrow \vec{p} - \frac{q}{c} \vec{A}(\vec{x}, t), \quad V(\vec{x}, t) \longrightarrow V(\vec{x}, t) + q\phi(\vec{x}, t).$$

II. Schrodinger equation for a charged particle in an external electromagnetic field

We first write down the time-dependent Schrodinger equation,

$$H |\psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle ,$$

where

$$H = \frac{1}{2m} \left(\vec{p} - \frac{q\vec{A}}{c} \right) \cdot \left(\vec{p} - \frac{q\vec{A}}{c} \right) + q\phi + V(\vec{x}, t).$$

For simplicity, we will set the external potential $V(\vec{x}, t)$ to zero, and assume that the electromagnetic potentials are time-independent. Then, the time-independent Schrodinger equation for stationary state solutions $|\psi\rangle$ is given by:

$$\frac{1}{2m} \left(\vec{p} - \frac{q\vec{A}}{c} \right)^2 |\psi\rangle = (E - q\phi) |\psi\rangle .$$

Comparing this with the time-independent Schrodinger equation for a free particle, one can introduce the *principle of minimal substitution* at this point by noting that the time-independent Schrodinger equation for a charged particle of charge q is obtained by the substitution:

$$\vec{p} \longrightarrow \vec{p} - \frac{q}{c} \vec{A}(\vec{x}, t), \quad E \longrightarrow E - q\phi(\vec{x}, t).$$

In the coordinate representation, we identify \vec{p} with the differential operator $-i\hbar\vec{\nabla}$. Hence, the time-independent Schrodinger equation is given by:

$$\boxed{\frac{1}{2m} \left[i\hbar\vec{\nabla} + \frac{q}{c} \vec{A}(\vec{x}) \right]^2 \psi(\vec{x}) + q\phi(\vec{x})\psi(\vec{x}) = E\psi(\vec{x}) .}$$

In obtaining the above result, we implicitly assumed that we should identify the canonical momentum \vec{p} [and *not* the mechanical momentum $m\vec{v}$] with the operator $-i\hbar\vec{\nabla}$. The momentum operator \vec{p} is called the *canonical* momentum because it satisfies the canonical commutation relations,

$$[x_i, p_j] = i\hbar\delta_{ij} .$$

This is one of the essential postulates of quantum mechanics. Had we tried to identify $m\vec{v}$ with $-i\hbar\vec{\nabla}$, we would have found that the resulting theory does not reduce to the classical limit as $\hbar \rightarrow 0$.

The Schrodinger equation written above can be expanded out:

$$\frac{-\hbar^2}{2m} \vec{\nabla}^2 \psi + \frac{iq\hbar}{mc} \vec{A} \cdot \vec{\nabla} \psi + \frac{iq\hbar}{2mc} \psi (\vec{\nabla} \cdot \vec{A}) + \frac{q^2}{2mc^2} \vec{A}^2 \psi + q\phi\psi = E\psi ,$$

where we have suppressed the coordinate arguments of the electromagnetic vector and scalar potentials and the wave function ψ . At this point, the equation can

be simplified by *choosing a gauge*. Given any \vec{A} and ϕ , one can perform a gauge transformation [cf. eq. (3)] such that the resulting \vec{A} and ϕ satisfy:

$$\boxed{\vec{\nabla} \cdot \vec{A} = 0, \quad \phi = 0, \quad \text{Coulomb gauge conditions}}$$

Suppose (\vec{A}, ϕ) are the initial vector and scalar potential. Making a gauge transformation,

$$\vec{A}' = \vec{A} + \vec{\nabla}\chi(\vec{x}, t), \quad \phi' = \phi - \frac{1}{c} \frac{\partial\chi(\vec{x}, t)}{\partial t}.$$

To ensure that the Coulomb gauge conditions are satisfied, we require that:

$$\vec{\nabla}^2\chi(\vec{x}, t) = -\vec{\nabla} \cdot \vec{A}(\vec{x}, t), \quad \frac{\partial\chi(\vec{x}, t)}{\partial t} = c\phi(\vec{x}, t).$$

One can always find a $\chi(\vec{x}, t)$ such that the above conditions are satisfied! By choosing such a $\chi(\vec{x}, t)$, it then follows that $\vec{\nabla} \cdot \vec{A}' = \phi' = 0$ as desired. Thus, the Schrodinger equation in the Coulomb gauge is given by:

$$\boxed{\frac{-\hbar^2}{2m} \vec{\nabla}^2\psi + \frac{iq\hbar}{mc} \vec{A} \cdot \vec{\nabla}\psi + \frac{q^2}{2mc^2} \vec{A}^2\psi + q\phi\psi = E\psi.}$$

III. Schrodinger equation for a charged particle in a uniform electromagnetic field

We can use the results obtained Section II to examine two cases.

1. A uniform electric field

In this case, it is *not* convenient to use the Coulomb gauge. Instead, we choose $\vec{A} = 0$ and $\vec{E} = -\vec{\nabla}\phi$. The Schrodinger equation becomes:

$$\frac{-\hbar^2}{2m} \vec{\nabla}^2\psi + q\phi\psi = E\psi,$$

which has the same form as the usual Schrodinger equation for a particle in a potential.

2. A uniform magnetic field

In this case, we will choose the Coulomb gauge. If \vec{B} is uniform in space and time-independent, then, one may choose:

$$\vec{A} = -\frac{1}{2}\vec{x} \times \vec{B}, \quad \phi = 0.$$

To check that this is correct, we use eq. (1) to compute \vec{E} and \vec{B} . Since \vec{A} is time-independent and $\phi = 0$, it follows that $\vec{E} = 0$. Next, we compute $\vec{B} = \vec{\nabla} \times \vec{A}$. Noting that:

$$A_x = -\frac{1}{2}(yB_z - zB_y), \quad A_y = -\frac{1}{2}(zB_x - xB_z), \quad A_z = -\frac{1}{2}(xB_y - yB_x),$$

one easily evaluates:

$$\begin{aligned}\vec{\nabla} \times \vec{A} &= \hat{x} \left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \right) + \hat{y} \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right) + \hat{z} \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) \\ &= \hat{x} B_x + \hat{y} B_y + \hat{z} B_z = \vec{B}.\end{aligned}$$

Furthermore, note that

$$\vec{\nabla} \cdot \vec{A} = -\frac{1}{2} \vec{\nabla} \cdot (\vec{x} \times \vec{B}) = 0,$$

which confirms that we have indeed chosen the Coulomb gauge. Thus, the time-independent Schrodinger equation reads:

$$\frac{-\hbar^2}{2m} \vec{\nabla}^2 \psi - \frac{iq\hbar}{2mc} (\vec{x} \times \vec{B}) \cdot \vec{\nabla} \psi + \frac{q^2}{8mc^2} (\vec{x} \times \vec{B})^2 \psi = E\psi.$$

This equation can be simplified by noting the vector identity:

$$(\vec{x} \times \vec{B}) \cdot \vec{\nabla} \psi = -\vec{B} \cdot (\vec{x} \times \vec{\nabla} \psi).$$

Hence,

$$-\frac{iq\hbar}{2mc} (\vec{x} \times \vec{B}) \cdot \vec{\nabla} \psi = -\frac{q}{2mc} \vec{B} \cdot \left(\vec{x} \times \frac{\hbar}{i} \vec{\nabla} \psi \right).$$

We identify the *canonical angular momentum operator*,

$$\vec{L} \equiv -i\hbar \vec{x} \times \vec{\nabla}. \quad (14)$$

This is to be distinguished from the mechanical angular momentum $\vec{x} \times (m\vec{v})$. You can check that the canonical angular momentum operators of eq. (14) satisfy the usual angular momentum commutation relations,

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k,$$

where there is an implicit sum over the repeated index $k \in \{1, 2, 3\}$. Hence, we can write:

$$-\frac{iq\hbar}{2mc} (\vec{x} \times \vec{B}) \cdot \vec{\nabla} \psi = -\frac{q}{2mc} \vec{B} \cdot \vec{L} \psi.$$

Finally, if we use the vector identity,

$$(\vec{x} \times \vec{B})^2 = r^2 \vec{B}^2 - (\vec{x} \cdot \vec{B})^2,$$

where $r \equiv |\vec{x}|$, then the time-independent Schrodinger equation for a charged particle of charge q in an external uniform magnetic field \vec{B} is given by:

$$\boxed{\frac{-\hbar^2}{2m} \vec{\nabla}^2 \psi - \frac{q}{2mc} \vec{B} \cdot \vec{L} \psi + \frac{q^2}{8mc^2} \left[r^2 \vec{B}^2 - (\vec{x} \cdot \vec{B})^2 \right] \psi = E\psi.} \quad (15)$$

IV. Schrodinger equation for a charged spin-1/2 particle in an electromagnetic field

So far, we have neglected spin. For a spin-1/2 particle, the wave function is a spinor of the form

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}.$$

Likewise, the Hamiltonian operator must be a 2×2 matrix.

To determine the correct Hamiltonian for a charged spin-1/2 particle in an electromagnetic field, we choose the Hamiltonian for a free uncharged spin-1/2 particle to be:

$$H = \frac{(\vec{\sigma} \cdot \vec{p})^2}{2m}. \quad (16)$$

Noting that $(\vec{\sigma} \cdot \vec{p})^2 = \vec{p}^2 \mathbf{I}$, where \mathbf{I} is the 2×2 identity matrix, we recover the expected free particle Hamiltonian. In order to obtain the Hamiltonian for a charged spin-1/2 particle, we apply the principle of minimal substitution to eq. (16).¹ Thus, we choose

$$H = \frac{1}{2m} \vec{\sigma} \cdot \left(\vec{p} - \frac{q\vec{A}}{c} \right) \vec{\sigma} \cdot \left(\vec{p} - \frac{q\vec{A}}{c} \right) + q\phi \mathbf{I}.$$

We can simplify the first term above by writing:

$$\begin{aligned} \vec{\sigma} \cdot \left(\vec{p} - \frac{q\vec{A}}{c} \right) \vec{\sigma} \cdot \left(\vec{p} - \frac{q\vec{A}}{c} \right) &= \sum_{ij} \sigma_i \sigma_j \left(p_i - \frac{qA_i}{c} \right) \left(p_j - \frac{qA_j}{c} \right) \\ &= \sum_{ijk} (\delta_{ij} \mathbf{I} + i\epsilon_{ijk} \sigma_k) \left(p_i - \frac{qA_i}{c} \right) \left(p_j - \frac{qA_j}{c} \right) \\ &= \left(\vec{p} - \frac{q\vec{A}}{c} \right)^2 \mathbf{I} - \frac{iq}{c} \sum_{ijk} \epsilon_{ijk} (p_i A_j + A_i p_j) \sigma_k, \quad (17) \end{aligned}$$

where we have used the sigma matrix identity,

$$\sigma_i \sigma_j = \mathbf{I} \delta_{ij} + i \sum_{k=1}^3 \epsilon_{ijk} \sigma_k.$$

Note that

$$\sum_{ij} \epsilon_{ijk} p_i p_j = \sum_{ij} \epsilon_{ijk} A_i A_j = 0,$$

since $\epsilon_{ijk} = -\epsilon_{jik}$ is a totally antisymmetric tensor.

¹If one applies the principle of minimal substitution to $H = (\vec{p}^2/(2m))\mathbf{I}$, one obtains a spin-independent Hamiltonian, which is in conflict with experiment. Remarkably, applying the principle of minimal substitution to eq. (16) yields a spin-dependent Hamiltonian, which is in very good agreement with experiment.

To evaluate the second term in eq. (17) above, we use

$$\sum_{ijk} \epsilon_{ijk} (p_i A_j + A_i p_j) \sigma_k = \sum_{ijk} \epsilon_{ijk} (p_i A_j - A_j p_i) \sigma_k,$$

where we have used the antisymmetry of ϵ_{ijk} followed by an appropriate relabeling of indices. Employing the operator identity (which is most easily checked in the coordinate representation),

$$p_i A_j - A_j p_i = [p_i, A_j] = -i\hbar \frac{\partial A_j}{\partial x_i},$$

it follows that

$$\sum_{ij} \epsilon_{ijk} (p_i A_j + A_i p_j) = \sum_{ij} \epsilon_{ijk} [p_i, A_j] = -i\hbar \sum_{ij} \epsilon_{ijk} \frac{\partial A_j}{\partial x_i} = -i\hbar B_k,$$

after recognizing that $\vec{B} = \vec{\nabla} \times \vec{A}$ implies that:

$$B_k = \sum_{ij} \epsilon_{ijk} \frac{\partial A_j}{\partial x_i}.$$

Consequently,

$$\vec{\sigma} \cdot \left(\vec{p} - \frac{q\vec{A}}{c} \right) \vec{\sigma} \cdot \left(\vec{p} - \frac{q\vec{A}}{c} \right) = \left(\vec{p} - \frac{q\vec{A}}{c} \right)^2 \mathbf{I} - \frac{\hbar q}{c} \vec{\sigma} \cdot \vec{B}.$$

Thus, the Hamiltonian for a charged spin-1/2 particle in an external electromagnetic field is:

$$H = \frac{1}{2m} \left(\vec{p} - \frac{q\vec{A}}{c} \right)^2 \mathbf{I} - \frac{\hbar q}{2mc} \vec{\sigma} \cdot \vec{B} + q\phi \mathbf{I}.$$

That is, if H_0 is the spin-independent part of the Hamiltonian, then

$$H = H_0 - \frac{q}{mc} \vec{S} \cdot \vec{B}, \quad (18)$$

where we have identified the spin-1/2 operator, $\vec{S} = \frac{1}{2}\hbar\vec{\sigma}$.

Let us apply the above results to obtain the time-independent Schrodinger equation for a charged spin-1/2 particle in a uniform magnetic field. Using eqs. (15) and (18), it follows that:

$$\frac{-\hbar^2}{2m} \vec{\nabla}^2 \psi - \frac{q}{2mc} \vec{B} \cdot (\vec{L} + 2\vec{S}) \psi + \frac{q^2}{8mc^2} \left[r^2 \vec{B}^2 - (\vec{x} \cdot \vec{B})^2 \right] \psi = E\psi.$$

Note especially the relative factor of 2 in $\vec{L} + 2\vec{S}$ above. This means that we have predicted that an elementary charged spin-1/2 particle has a g -factor equal to 2. In more general circumstances, $\vec{L} + 2\vec{S}$ in the above equation should be replaced by $\vec{L} + g\vec{S}$, where g is determined from experiment.