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 $\vec{\boldsymbol{E}}$ and magnetic field $\vec{\boldsymbol{B}}$. Gaussian (or cgs) units are employed for electromagnetic quantities. It is convenient to introduce the vector potential $\vec{\boldsymbol{A}}$ and the scalar potential ϕ:

$$\vec{\boldsymbol{B}} = \vec{\boldsymbol{\nabla}} \times \vec{\boldsymbol{A}}\,, \qquad \vec{\boldsymbol{E}} = -\vec{\boldsymbol{\nabla}}\phi - \frac{1}{c}\frac{\partial \vec{\boldsymbol{A}}}{\partial t}\,. \tag{1}$$

These equations encode two of the four Maxwell equations,

$$\vec{\boldsymbol{\nabla}}\cdot\vec{\boldsymbol{B}} = 0\,, \qquad \vec{\boldsymbol{\nabla}} \times \vec{\boldsymbol{E}} = -\frac{1}{c}\frac{\partial \vec{\boldsymbol{B}}}{\partial t}\,, \tag{2}$$

due to the vector identities

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

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

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

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

called *gauge transformations* leave the physical electromagnetic fields, $\vec{\boldsymbol{E}}$ and $\vec{\boldsymbol{B}}$, 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:

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

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

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

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:

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

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:

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

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

Eq. (6) is equivalent to:

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

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

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

which we can rewrite as:

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

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

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

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

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

Inserting this result in eq. (9) yields:

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

Next, we make use of the vector identity:

$$\left[\vec{\boldsymbol{v}}\times(\vec{\boldsymbol{\nabla}}\times\vec{\boldsymbol{A}})\right]_i = \vec{\boldsymbol{v}}\boldsymbol{\cdot}\frac{\partial\vec{\boldsymbol{A}}}{\partial x_i} - (\vec{\boldsymbol{v}}\boldsymbol{\cdot}\vec{\boldsymbol{\nabla}})A_i\,. \tag{11}$$

This should remind you of the BAC–CAB rule used for computing the triple cross-product: $\vec{\boldsymbol{A}}\times(\vec{\boldsymbol{B}}\times\vec{\boldsymbol{C}}) = \vec{\boldsymbol{B}}(\vec{\boldsymbol{A}}\boldsymbol{\cdot}\vec{\boldsymbol{C}}) - \vec{\boldsymbol{C}}(\vec{\boldsymbol{A}}\boldsymbol{\cdot}\vec{\boldsymbol{B}})$. 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 $\vec{\boldsymbol{x}}$. However, it is straightforward to prove eq. (11) by employing a well-known identity involving the product of two Levi Civita tensors:

$$\left[\vec{\boldsymbol{v}}\times(\vec{\boldsymbol{\nabla}}\times\vec{\boldsymbol{A}})\right]_i = \epsilon_{ijk}v_j\epsilon_{k\ell m}\frac{\partial A_m}{\partial x_\ell} = (\delta_{i\ell}\delta_{jm} - \delta_{im}\delta_{j\ell})v_j\frac{\partial A_m}{\partial x_\ell} = \vec{\boldsymbol{v}}\boldsymbol{\cdot}\frac{\partial\vec{\boldsymbol{A}}}{\partial x_i} - (\vec{\boldsymbol{v}}\boldsymbol{\cdot}\vec{\boldsymbol{\nabla}})A_i\,, \tag{12}$$

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

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

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

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

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 $V(\vec{\boldsymbol{x}},t)$ that is unrelated to the external electromagnetic field, then we should use the more general Hamiltonian,

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

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:

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

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

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

For simplicity, we will set the external potential $V(\vec{\boldsymbol{x}},t)$ 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:

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

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:

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

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

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

In obtaining the above result, we implicitly assumed that we should identify the canonical momentum $\vec{\boldsymbol{p}}$ [and *not* the mechanical momentum $m\vec{\boldsymbol{v}}$] with the operator $-i\hbar\vec{\boldsymbol{\nabla}}$. The momentum operator $\vec{\boldsymbol{p}}$ 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 $m\vec{\boldsymbol{v}}$ with $-i\hbar\vec{\boldsymbol{\nabla}}$, we would have found that the resulting theory does not reduce to the classical limit as $\hbar \to 0$.

The Schrodinger equation written above can be expanded out:

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

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 $\vec{\boldsymbol{A}}$ and ϕ, one can perform a gauge transformation [cf. eq. (3)] such that the resulting $\vec{\boldsymbol{A}}$ and ϕ satisfy:

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

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

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

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

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

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

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

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 $\vec{\boldsymbol{A}} = 0$ and $\vec{E} = -\vec{\boldsymbol{\nabla}}\phi$. The Schrodinger equation becomes:

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

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 $\vec{\boldsymbol{B}}$ is uniform in space and time-independent, then, one may choose:

$$\vec{\boldsymbol{A}} = -\tfrac{1}{2}\vec{\boldsymbol{x}}\times\vec{\boldsymbol{B}}\,, \qquad\qquad \phi = 0\,.$$

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

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

one easily evaluates:

$$\vec{\nabla} \times \vec{A} = \hat{x}\left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}\right) + \hat{y}\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right) + \hat{z}\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right)$$

$$= \hat{x}B_x + \hat{y}B_y + \hat{z}B_z = \vec{B}\,.$$

Furthermore, note that

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

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*,

$$\vec{L} \equiv -i\hbar\vec{x}\times\vec{\nabla}\,. \tag{14}$$

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:

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

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:

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

Noting that $(\vec{\boldsymbol{\sigma}}\boldsymbol{\cdot}\vec{\boldsymbol{p}})^2 = \vec{\boldsymbol{p}}^{\,2}\mathbf{I}$, 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

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

We can simplify the first term above by writing:

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

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

$$\sum_{ij}\epsilon_{ijk}p_ip_j = \sum_{ij}\epsilon_{ijk}A_iA_j = 0 ,$$

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

[1] If one applies the principle of minimal substitution to $H = (\vec{\boldsymbol{p}}^{\,2}/(2m))\mathbf{I}$, 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 $\vec{\boldsymbol{B}} = \vec{\boldsymbol{\nabla}} \times \vec{\boldsymbol{A}}$ implies that:

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

Consequently,

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

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

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

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

$$H = H_0 - \frac{q}{mc} \vec{\boldsymbol{S}}\boldsymbol{\cdot}\vec{\boldsymbol{B}} \,, \tag{18}$$

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

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:

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

Note especially the relative factor of 2 in $\vec{\boldsymbol{L}} + 2\vec{\boldsymbol{S}}$ 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, $\vec{\boldsymbol{L}} + 2\vec{\boldsymbol{S}}$ in the above equation should be replaced by $\vec{\boldsymbol{L}} + g\vec{\boldsymbol{S}}$, where g is determined from experiment.