The (Quantum) Hamiltonian for a Charged Particle in a Given Electromagnetic Field

AnthonyMakesVideos

1 Hamiltonian, Classical Equations

Consider a charged particle in a given electromagnetic field and disregard the fields produced by the given charged particle.

Denote the vector potential as $\mathbf{a}(x, y, z, t)$, the scalar potential as $\phi(x, y, z, t)$, and let V denote part of the potential energy which is of non-electromagnetic origin for a Hamiltonian of

$$H = \frac{\left(\mathbf{p} - \frac{e}{c}\mathbf{a}\right)^2}{2m} + V(\mathbf{x}) + e\phi. \tag{1}$$

V could include, for example, gravitational potential energy or forces from protons or neutrons inside a nucleus. In this context, the electromagnetic force is considered dominant, so V might be zero or small, and the separation of V without its total omission keeps the treatment general.

To motivate (1), begin with a Lagrangian

$$L(q_1, \ldots, q_n, \dot{q}_1, \ldots, \dot{q}_n, t) \tag{2}$$

which is a function of generalized coordinates q_i, their velocities $\dot{q}_i$, and possibly explicit time dependence.

The equations of motion come from the Euler-Lagrange equations

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_i}\right) = \frac{\partial L}{\partial q_i}. \tag{3}$$

For each coordinate, define

$$p_i := \frac{\partial L}{\partial \dot{q}_i} \quad (i = 1, \ldots, n). \tag{4}$$

This provides a map

$$(q, \dot{q}, t) \mapsto (q, p, t) \tag{5}$$

from velocity space to momentum space. For the theory to be well-behaved, this map is assumed to be locally invertible i.e., given (q, p, t) the velocities $\dot{q}_i = \dot{q}_i(q, p, t)$ can be solved for.

This is true for regular (non-degenerate) Lagrangians as is the electromagnetic Lagrangian being discussed here.

The Hamiltonian is defined by the Legendre transform of L from (2) with respect to the velocity variables:

$$H(q, p, t) := \sum_{i=1}^{n} p_i \dot{q}_i(q, p, t) - L(q, \dot{q}_i(q, p, t)). \tag{6}$$

(7) in effect takes the "intercept" term $\sum p_i \dot{q}_i$ which is linear in the velocities and then subtracts the original function L evaluated at the velocities that correspond to the given p.

This is the standard Legendre transform $H = L^{\star} L$ in the velocity variables which geometrically converts a function of $\dot{q}_i$ into a function of the slope p.

Note that $p_i = \dfrac{\partial L}{\partial \dot{q}_i}$ and proceed to compute $\mathrm{d}H$:

$$\mathrm{d}H = \sum_i (\dot{q}_i \mathrm{d}p_i + p_i \mathrm{d}\dot{q}_i) - \left(\sum_i \frac{\partial L}{\partial q_i} \mathrm{d}q_i + \sum_i \frac{\partial L}{\partial \dot{q}_i} \mathrm{d}\dot{q}_i + \frac{\partial L}{\partial t} \mathrm{t} \right). \tag{7}$$

Since $p_i = \dfrac{\partial L}{\partial \dot{q}_i}$, the terms involving $\mathrm{d}\dot{q}_i$ cancel:

$$\mathrm{d}H = \sum_i \dot{q}_i \mathrm{d}p_i - \sum_i \frac{\partial L}{\partial q_i} - \frac{\partial L}{\partial t} \mathrm{d}t. \tag{8}$$

H is regarded as a function of the independent variables (q, p, t), so it is also permissible to write

$$\mathrm{d}H = \sum_i \frac{\partial H}{\partial q_i} \mathrm{d}q_i + \sum_i \frac{\partial H}{\partial p_i} \mathrm{d}p_i + \frac{\partial H}{\partial t} \mathrm{d}t. \tag{9}$$

Comparing the coefficients of (9) and (10) immediately yields Hamilton's canonical equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \tag{10}$$

together with the identity $\dfrac{\partial H}{\partial t} = -\dfrac{\partial L}{\partial t}$.

The pair (q, p) lives on the cotangent bundle $T^{\star}Q$ of the configuration manifold Q.

Hamilton's equations are thus the flow of the Hamiltonian vector field defined by the symplectic form $\omega = \sum \mathrm{d}q_i \wedge \mathrm{d}p_i$.

The Hamiltonian is the Legendre transform of the Lagrangian with respect to the velocity variables; the canonical equations are simply the statement that the coordinates and momenta are conjugate with respect to the symplectic structure that this transform naturally produces.

The x-component velocity $\dot{\mathbf{x}}$ will now be derived from the Hamiltonian (1) and the canonical equations (10).

First, the squared term on the right hand side of (1) is expanded:

$$\left(\mathbf{p} - \frac{e}{c}\mathbf{a}\right)^2 = \left(\mathbf{p}_x - \frac{e}{c}\mathbf{a}_x\right)^2 + \left(\mathbf{p}_y - \frac{e}{c}\mathbf{a}_y\right)^2 + \left(\mathbf{p}_z - \frac{e}{c}\mathbf{a}_x\right)^2. \tag{11}$$

Next, per the x-component (the y and z components are identical), $\dfrac{\partial H}{\partial p_x}$ will be computed. Only the first term on the right hand side of (1) depends on p_x; V and ϕ do not depend on the momentum.

$$\dot{\mathbf{x}} = \frac{\partial H}{\partial \mathbf{p}_x} = \frac{1}{2m} \cdot 2\left(\mathbf{p}_x - \frac{e}{c}\mathbf{a}_x\right) \cdot 1 = \frac{1}{m}\left(\mathbf{p}_x - \frac{e}{c}\mathbf{a}_x\right). \tag{12}$$

The canonical momentum is thus

$$\mathbf{p} = m\dot{\mathbf{x}} + \frac{e}{c}\mathbf{a}(\mathbf{x}). \tag{13}$$

The Lorentz force law will now be derived from the Hamiltonian (1). Denote the mechanical momentum by $\pi = \mathbf{p} - \frac{e}{c}\mathbf{a}$ so that $\mathbf{v} = \dot{\mathbf{r}} = \pi/m$.

By symmetry, (12) may be written as

$$\dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i} = \frac{1}{m}\left(\mathbf{p}_i - \frac{e}{c}\mathbf{a}_i\right) \Rightarrow \pi = m\mathbf{v}. \tag{14}$$

From (10), the canonical momentum can be written

$$\mathbf{p}_i = -\frac{\partial H}{\partial \mathbf{r}_i}. \tag{15}$$

Begin evaluating (15) by computing the partial derivative on the right-hand side

$$\frac{\partial H}{\partial \mathbf{r}_i} = \sum_j \frac{\pi_j}{m}\left(-\frac{e}{c}\frac{\partial \mathbf{a}_j}{\partial \mathbf{r}_i}\right) + \frac{\partial V}{\partial \mathbf{r}_i} + e\frac{\partial \phi}{\partial \mathbf{r}_i} \Rightarrow \mathbf{p}_i = \frac{e}{c}\sum_j \mathbf{v}_j \frac{\partial \mathbf{a}_j}{\partial \mathbf{r}_i} - \frac{\partial V}{\partial \mathbf{r}_i} - e\frac{\partial \phi}{\partial \mathbf{r}_i}. \tag{16}$$

The force is given by the rate of change of mechanical momentum

$$m\dot{\mathbf{v}}_i = \frac{\mathrm{d}\pi_i}{\mathrm{d}t} = \mathbf{p}_i - \frac{e}{c}\frac{\mathrm{d}\mathbf{a}_i}{\mathrm{d}t}. \tag{17}$$

Note the total (convective) derivative along the trajectory is given by

$$\frac{\mathrm{d}\mathbf{a}_i}{\mathrm{d}t} = \frac{\partial \mathbf{a}_i}{\partial t} + \sum_j \mathbf{v}_j \frac{\partial \mathbf{a}_i}{\partial \mathbf{r}_j} = \frac{\partial \mathbf{a}_i}{\partial t} + (\mathbf{v}\cdot\nabla)\mathbf{a}_i. \tag{18}$$

Substitute (18) and the far right-hand side of (16) into (17) to obtain

$$m\dot{\mathbf{v}}_i = \left[\frac{e}{c}\sum_j \mathbf{v}_j \frac{\partial \mathbf{a}_j}{\partial \mathbf{r}_i} - \frac{\partial V}{\partial \mathbf{r}_i} - e\frac{\partial \phi}{\partial \mathbf{r}_i}\right] - \frac{e}{c}\frac{\partial \mathbf{a}_i}{\partial t} - \frac{e}{c}\sum_j \mathbf{v}_j \frac{\partial \mathbf{a}_i}{\partial \mathbf{r}_j}. \tag{19}$$

(19) can be re-grouped according to the magnetic (velocity-dependent) terms as

$$m\dot{\mathbf{v}}_i = -\frac{\partial V}{\partial \mathbf{r}_i} - e\frac{\partial \phi}{\partial \mathbf{r}_i} - \frac{e}{c}\frac{\partial \mathbf{a}_i}{\partial t} + \frac{e}{c}\sum_j \mathbf{v}_j \left(\frac{\partial \mathbf{a}_j}{\partial \mathbf{r}_i} - \frac{\partial \mathbf{a}_i}{\partial \mathbf{r}_j}\right). \tag{20}$$

By the definition of the electric field in terms of the potentials,

$$\mathcal{E}_i = -\frac{\partial \phi}{\partial \mathbf{r}_i} - \frac{1}{c}\frac{\partial \mathbf{a}_i}{\partial t}, \tag{21}$$

the first three terms on the right-hand side of (20) are equal to $-\partial V/\partial \mathbf{r}_i + e\mathcal{E}_i$.

Recall that the Levi-Civita symbol ϵ_{ijk} is a completely antisymmetric tensor is defined as

$$\epsilon_{ijk} = \begin{cases} 1| \ (i,j,k) \text{ is an even permutation of } (1,2,3) \\ -1 \mid (i,j,k) \text{ is an odd permutation of } (1,2,3) \\ 0 \text{ otherwise.} \end{cases} \tag{22}$$

The Levi-Civita symbol thus encodes the cross product in general via

$$(\mathbf{u} \times \mathbf{w})_i = \sum_{j,k=1}^{3} \epsilon_{ijk} \mathbf{u}_j \mathbf{w}_k \tag{23}$$

and the curl of the magnetic field via

$$\mathcal{B}_k = (\nabla \times \mathbf{a})_k = \sum_{l,m} \epsilon_{klm} \frac{\partial \mathbf{a}_m}{\partial \mathbf{r}_l}. \tag{24}$$

Consider representing the cross-product of the velocity vector of the charged particle $\mathbf{v}$ and the magnetic field $\mathcal{B}$ via (23) and (24)

$$(\mathbf{v} \times \mathcal{B})_i = \sum_{j,k} \epsilon_{ijk} \mathbf{v}_j \mathcal{H}_k = \sum_{j,k,l,m} \epsilon_{ijk} \epsilon_{klm} \mathbf{v}_j \frac{\partial \mathbf{a}_m}{\partial \mathbf{r}_l}. \tag{25}$$

Furthermore, note the identity for the product of two Levi-Civita symbols

$$\epsilon_{ijk}\epsilon_{klm} = \delta_{il}\delta_{jm} - \delta_{im}\delta_{jl} \tag{26}$$

where δ is the Kronecker delta.

Substituting the identity (26) into (25) yields

$$(\mathbf{v} \times \mathcal{B})_i = \sum_{j,l,m} \mathbf{v}_j (\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}) \frac{\partial \mathbf{a}_m}{\partial \mathbf{r}_l}. \tag{27}$$

Expanding the first term on the right-hand side of (27) yields

$$\sum_{j,l,m} \mathbf{v}_j \delta_{il}\delta_{jm}\partial_l \mathbf{a}_m = \sum_j \mathbf{v}_j \partial_i \mathbf{a}_j \text{ because } \delta_{il} \text{ sets } l = i \text{ and } \delta_{jm} \text{ sets } m = j. \tag{28}$$

Expanding the second term on the right-hand side of (27) yields

$$\sum_{j,l,m} \mathbf{v}_j \delta_{im}\delta_{jl}\partial_l \mathbf{a}_m = \sum_l \mathbf{v}_l \partial_l \mathbf{a}_i \text{ because } \delta_{im} \text{ sets } m = i \text{ and } \delta_{jl} \text{ sets } j = l. \tag{29}$$

Combining (28) and (29), and relabeling the dummy index $l \to j$ in (29) thus re-writes (27) as

$$(\mathbf{v} \times \mathcal{B})_i = \sum_j \mathbf{v}_j \frac{\partial \mathbf{a}_j}{\partial \mathbf{r}_i} - \sum_j \mathbf{v}_j \frac{\partial \mathbf{a}_i}{\partial \mathbf{r}_j}. \tag{30}$$

Therefore, combining (21) and (30) to re-write (20) yields

$$m\frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2} = -\nabla V + e\mathcal{E} + \frac{e}{c}\mathbf{v} \times \mathcal{B} \tag{31}$$

where

$$\mathcal{E} = -\nabla\phi - \frac{1}{c}\frac{\partial \mathbf{a}}{\partial t}, \quad \mathcal{B} = \nabla \times \mathbf{a}, \tag{32}$$

which recovers the correct classical equations of motion.

2 Quantum-mechanical Hamiltonian

To obtain the quantum-mechanical Hamiltonian operator, replace the canonical momentum $\mathbf{p}$ with the operator $(\hbar/i)\nabla$ in (1) to yield

$$\widehat{H} = \frac{\left(\frac{\hbar}{i}\nabla - \frac{e}{c}\mathbf{a}\right)^2}{2m} + e\phi + V = \frac{-\hbar^2}{2m}\nabla^2 + e\phi + V - \frac{\hbar e}{2mci}(\mathbf{a}\cdot\nabla + \nabla\cdot\mathbf{a}) + \frac{e^2}{2mc^2}\mathbf{a}^2. \tag{33}$$

Next, (33) will be shown to be Hermitian. If the above Hamiltonian is Hermitian, probability is conserved.

$\widehat{H}$ may be written

$$\widehat{H} = \frac{-\hbar^2}{2m}\nabla^2 + e\phi + V + \widehat{L} + \frac{e^2}{2mc^2}\mathbf{a}^2 \tag{34}$$

where

$$\widehat{L}\psi = kD\psi, \quad D\psi := \mathbf{a}\cdot\nabla\psi + (\nabla\cdot\mathbf{a})\psi, \quad k = \frac{-\hbar e}{2mci} = i\mu \tag{35}$$

with $\mu = \dfrac{\hbar e}{2mc}$. Since μ is real, $k^\star = -k$.

Note that for any real function $f(r)$,

$$\langle\psi|f(\phi)\rangle = \int \psi^\star f\phi \,\mathrm{d}^3r = \int (f\psi)^\star\phi \,\mathrm{d}^3r = \langle f\psi|\phi\rangle. \tag{36}$$

Therefore, $e\phi + V$ and $\dfrac{e^2}{2mc^2}\mathbf{a}^2$ are Hermitian.

Recall Green's first identity

$$\int_\Omega \psi^\star\nabla^2\phi \,\mathrm{d}V = \int_{\partial\Omega} \psi^\star\frac{\partial\phi}{\partial\mathbf{n}} \,\mathrm{d}S - \int_\Omega \nabla\psi^\star\cdot\nabla\phi \,\mathrm{d}V. \tag{37}$$

Applying Green's first identity to a large volume Ω and letting $\Omega\to\mathbb{R}^3$, the surface term vanishes. Taking the complex conjugate and interchanging $\psi\leftrightarrow\phi$ yields

$$\int \psi^\star\nabla^2\phi \,\mathrm{d}^3r = -\int \nabla\psi^\star\cdot\nabla\phi \,\mathrm{d}^3r = \left(\int \phi^\star\nabla^2\psi \,\mathrm{d}^3r\right)^\star. \tag{38}$$

Hence

$$\langle\psi|\nabla^2\phi\rangle = \langle\nabla^2\psi|\phi\rangle^\star, \tag{39}$$

and the term $\dfrac{-\hbar^2}{2m}\nabla^2$ is Hermitian:

$$\langle\psi|\frac{-\hbar^2}{2m}\nabla^2\phi\rangle = \langle\frac{-\hbar^2}{2m}\nabla^2\psi|\phi\rangle. \tag{40}$$

Next, it will be shown that $D^\dagger = -D$. Compute

$$\langle\psi|D\phi\rangle = \int \psi^\star(\mathbf{a}\cdot\nabla\phi)\ \mathrm{d}^3r + \int \psi^\star(\nabla\cdot\mathbf{a})\phi\ \mathrm{d}^3r. \tag{41}$$

By the divergence theorem, the surface term vanishes thus proceed by performing integration by parts on the first term

$$\int \psi^\star(\mathbf{a}\cdot\nabla\phi)\ \mathrm{d}^3r = -\int \phi\nabla\cdot(\psi^\star\mathbf{a})\ \mathrm{d}^3r = -\int \phi(\mathbf{a}\cdot\nabla\psi^\star)\ \mathrm{d}^3r - \int \phi\psi^\star(\nabla\cdot\mathbf{a})\ \mathrm{d}^3r. \tag{42}$$

Therefore

$$\langle\psi|D\phi\rangle = -\int(\mathbf{a}\cdot\nabla\psi^\star)\phi\ \mathrm{d}^3r - \int \psi^\star(\nabla\cdot\mathbf{a})\phi\ \mathrm{d}^3r = -\int\left[\mathbf{a}\cdot\nabla\psi^\star + \psi^\star(\nabla\cdot\mathbf{a})\right]\phi\ \mathrm{d}^3r. \tag{43}$$

Since $\mathbf{a}$ is real-valued, $\mathbf{a}\cdot\nabla\psi^\star = (\mathbf{a}\cdot\nabla\psi)^\star$. Thus,

$$\langle\psi|D\phi\rangle = \int\left[-(\mathbf{a}\cdot\nabla\psi) - (\nabla\cdot\mathbf{a})\psi\right]^\star\phi\ \mathrm{d}^3r = \langle -D\psi|\phi\rangle. \tag{44}$$

Therefore, $D^\dagger = -D$. Next, since $k^\star = -k$, the adjoint of $\widehat{L}$ is

$$\widehat{L}^\dagger = (kD)^\dagger = D^\dagger k^\star = (-D)(-k) = kD = \widehat{L}, \tag{45}$$

hence $\widehat{L}$ is Hermitian

$$\langle\psi|\widehat{L}\phi\rangle = \langle\widehat{L}\psi|\phi\rangle. \tag{46}$$

All terms of $\widehat{H}$ are seen to be Hermitian, so $\widehat{H}$ itself is Hermitian.

3 Probability Current

Since (33) is Hermitian, probability is conserved, but nevertheless the change of probability will be calculated to obtain an expression for the probability current.

Using $i\hbar(\partial\psi/\partial t) = \widehat{H}\psi$ obtains the following formulation of the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \widehat{H}\psi = \frac{1}{2m}\left(-i\hbar\nabla - \frac{e}{c}\mathbf{a}\right)^2\psi + (e\phi + V)\psi. \tag{47}$$

Taking the complex conjugate of (47) obtains

$$-i\hbar\frac{\partial\psi^\star}{\partial t}=\frac{1}{2m}\left(i\hbar\nabla-\frac{e}{c}\mathbf{a}\right)^2\psi^\star+(e\phi+V)\psi^\star. \tag{48}$$

From the probability density $P=\psi^\star\psi$, then the probability current is given by

$$\frac{\partial P}{\partial t}=\frac{\partial}{\partial t}(\psi^\star\psi)=\psi^\star\frac{\partial\psi}{\partial t}+\psi\frac{\partial\psi^\star}{\partial t}. \tag{49}$$

Solving for the time derivatives from (47) and (48) yields

$$\frac{\partial\psi}{\partial t}=\frac{1}{i\hbar}\widehat{H}\psi,\quad \frac{\partial\psi^\star}{\partial t}=\frac{-1}{i\hbar}\widehat{H}^\star\psi^\star. \tag{50}$$

Thus, (49) becomes

$$\begin{aligned}\frac{\partial P}{\partial t}&=\psi^\star\left(\frac{1}{i\hbar}\widehat{H}\psi\right)+\psi\left(\frac{-1}{i\hbar}\widehat{H}^\star\psi^\star\right)\\&=\frac{1}{i\hbar}\left(\psi^\star\widehat{H}\psi-\psi\widehat{H}^\star\psi^\star\right).\end{aligned} \tag{51}$$

Inserting (33) into (51), keeping in mind that real terms will cancel when the subtraction is taken, yields

$$\begin{aligned}\frac{\partial P}{\partial t}=&-\frac{\psi}{2mi\hbar}\left(-\frac{\hbar}{i}\nabla-\frac{e}{c}\mathbf{a}\right)\left(-\frac{\hbar}{i}\nabla-\frac{e}{c}\mathbf{a}\right)\psi^\star\\&+\frac{\psi^\star}{2mi\hbar}\left(\frac{\hbar}{i}\nabla-\frac{e}{c}\mathbf{a}\right)\cdot\left(\frac{\hbar}{i}\nabla-\frac{e}{c}\mathbf{a}\right)\psi.\end{aligned} \tag{52}$$

Denote $\pi:=-i\hbar\nabla-\frac{e}{c}\mathbf{a}$ and $\pi^\star:=+i\hbar\nabla-\frac{e}{c}\mathbf{a}$ so that (52) can be written as

$$\frac{\mathrm{d}P}{\mathrm{d}t}=\frac{-\psi}{2mi\hbar}(\pi^\star\cdot\pi^\star\psi^\star)+ \tag{53}$$

$$\frac{\psi^\star}{2mi\hbar}(\pi\cdot\pi\psi). \tag{54}$$

(53) expands to

$$\frac{-i\hbar}{2m}\psi\nabla^2\psi^\star+\frac{e}{2mc}(\psi\nabla(\mathbf{a}\psi^\star)+\psi\mathbf{a}\nabla\psi^\star)+\frac{ie^2}{2mc^2\hbar}\psi(\mathbf{a}\cdot\mathbf{a})\psi^\star \tag{55}$$

and (54) expands to

$$\frac{i\hbar}{2m}\psi^\star\nabla^s\psi + \frac{e}{2mc}(\psi^\star\nabla(\mathbf{a}\psi) + \psi^\star\mathbf{a}\nabla\psi) - \frac{ie^2}{2mc^2\hbar}\psi^\star(\mathbf{a}\cdot\mathbf{a})\psi. \tag{56}$$

Adding (55) and (56) yields

$$\frac{i\hbar}{2m}(\psi^\star\nabla^2\psi - \psi\nabla^2\psi^\star) \tag{57}$$
$$+ \frac{e}{2mc}(\psi^\star\nabla(\mathbf{a}\psi) + \psi\nabla(\mathbf{a}\psi^\star)) \tag{58}$$
$$+ \frac{e}{2mc}(\psi^\star\mathbf{a}\nabla\psi + \psi\mathbf{a}\nabla\psi^\star) \tag{59}$$
$$+ \frac{ie^2}{2mc^2\hbar}(-\psi^\star(\mathbf{a}\cdot\mathbf{a})\psi + \psi(\mathbf{a}\cdot\mathbf{a})\psi^\star). \tag{60}$$

Note that (60) equals zero. Using the identity $\nabla\cdot(\mathbf{a}\psi) = (\nabla\cdot\mathbf{a})\psi + \mathbf{a}\cdot\nabla\psi$, (58) becomes

$$\frac{e}{2mc}(\psi^\star((\nabla\cdot\mathbf{a})\psi + \mathbf{a}\cdot\nabla\psi) + \psi((\nabla\cdot\mathbf{a})\psi^\star + \mathbf{a}\cdot\nabla\psi^\star)). \tag{61}$$

Adding (61) and (59) results in

$$\frac{e}{mc}(\psi^\star\psi(\nabla\cdot\mathbf{a}) + \psi^\star\mathbf{a}\cdot\nabla\psi + \psi\mathbf{a}\cdot\nabla\psi^\star). \tag{62}$$

The identity $\nabla(\psi^\star\psi) = \psi^\star\nabla\psi + \psi\nabla\psi^\star$ shows that from (62),

$$\psi^\star\mathbf{a}\cdot\nabla\psi + \psi\mathbf{a}\cdot\nabla\psi^\star = \mathbf{a}\cdot\nabla(\psi^\star\psi). \tag{63}$$

Furthermore, the identity $\nabla\cdot(\psi^\star\psi\mathbf{a}) = \psi^\star\psi(\nabla\cdot\mathbf{a}) + \mathbf{a}\cdot\nabla\psi^\star\psi$ in conjunction with (63) indicates that (62) is equivalent to

$$\nabla\cdot\left(\frac{e}{mc}\mathbf{a}\psi^\star\psi\right). \tag{64}$$

Re-writing (57) as $\nabla\cdot\left[\frac{i\hbar}{2m}(\psi^\star\nabla\psi - \psi\nabla\psi^\star)\right]$ and combining this with (64) results in

$$\frac{\partial P}{\partial t} = \nabla\cdot\left[\frac{\hbar}{2mi}(\psi\nabla\psi^\star - \psi^\star\nabla\psi) + \frac{e}{mc}\mathbf{a}\psi^\star\psi\right] \tag{65}$$

Rearrangement of (65) yields

$$\frac{\partial P}{\partial t} + \nabla \cdot \left[\frac{\hbar}{2mi} \left(\psi^\star \nabla \psi - \psi \nabla \psi^\star \right) - \frac{e}{mc} \mathbf{a} \psi^\star \psi \right] = 0 \tag{66}$$

and writing

$$\mathbf{S} = \frac{\hbar}{2mi} (\psi^\star \nabla \psi - \psi \nabla \psi^\star) - \frac{e}{mc} \mathbf{a} \psi^\star \psi \tag{67}$$

thus obtains

$$\frac{\partial P}{\partial t} + \nabla \cdot \mathbf{s} = 0. \tag{68}$$

4 Classical Limit

Note the general Ehrenfest formula for any operator A,

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle A \rangle = \frac{i}{\hbar} \langle [H, A] \rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle. \tag{69}$$

Ehrenfest's Theorem specifically relates the time derivative of the expectation values of the position and momentum operators x and p to the expectation value of the force $F = -V(x)$ on a massive particle moving in a scalar potential $V(x)$.

This theorem is a special case of the more general relation (69) between the expectation of any quantum mechanical operator and the expectation of the commutator of that operator with the Hamiltonian of the system.

It can be shown using Ehrenfest's formula that Schrödinger's equation approaches Newton's laws of motion when a vector potential is present.

Specifically, it will now be shown that the average values of x and p satisfy the classical equations of motion when a vector potential only is present.

Let $\pi := \mathbf{p} - \frac{e}{c} \mathbf{a}$ denote the mechanical kinetic momentum operator, and for consistency note that $\mathbf{p} = -i\hbar\nabla$.

The quantum-mechanical Hamiltonian (1) in terms of $r = \langle x_j \rangle$ in the absence of scalar potential (i.e., $\phi = 0$) and the absence of potentials of non-EM origin (i.e., $V = 0$) is then

$$H = \frac{\left(\mathbf{p} - \frac{e}{c}\mathbf{a}(r,t)\right)^2}{2m} = \frac{1}{2m}(\pi)^2 = \frac{1}{2m}\sum_j \pi_j^2 \tag{70}$$

First, consider the position operator r. This has no explicit time dependence, so

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle r \rangle = \frac{i}{\hbar}\langle [H, r] \rangle. \tag{71}$$

To compute the commutator $[H, r]$, notice that

$$[H, r] = \frac{1}{2m}\left[\pi^2, r\right] = \frac{1}{2m}\sum_j \left[\pi_j^2, x_i\right], \tag{72}$$

so $\left[\pi^2, r\right]$ must be computed. It is enough to find $[\pi_j, x_i]$ first.

As π is written, the scalar potential $\mathbf{a}(r,t)$ acts as a multiplication operator as a function of r and as such commutes with r, i.e., $[\mathbf{a}_j(r), x_i] = 0$.

Therefore, recalling that the canonical commutation relation for the canonical momentum is $[\mathbf{p}_k, x_l] = -i\hbar\delta_{kl}$, the commutator $[\pi_j, x_i]$ is given by

$$[\pi_j, x_i] = \left[\mathbf{p}_j, x_i\right] - \frac{e}{c}\left[\mathbf{a}_j, x_i\right] = -i\hbar\delta_{ij}. \tag{73}$$

Using the identity $[AB, C] = A[B, C] + [A, C]B$, the commutator $\left[\pi_j^2, x_i\right]$ can be computed

$$\left[\pi_j^2, x_i\right] = \pi_j\left[\pi_j, x_i\right] + \left[\pi_j, x_i\right]\pi_j \tag{74}$$

$$= \pi_j(-i\hbar\delta_{ij}) + (-i\hbar\delta_{ij})\pi_j = -i\hbar\delta_{ij}(\pi_j + \pi_j) \tag{75}$$

$$= -2i\hbar\delta_{ij}\pi_j \tag{76}$$

Plugging (76) back into the sum of (72) results in

$$[H, x_i] = \frac{1}{2m}\sum_j(-2i\hbar\delta_{ij}\pi_j) = \frac{-i\hbar}{m}\pi_i. \tag{77}$$

Plugging (77) back into (71) yields

$$\frac{\mathrm{d}\langle r\rangle}{\mathrm{d}t} = \frac{\langle \pi\rangle}{m} = \left\langle \frac{\mathbf{p} - \frac{e}{c}\mathbf{a}(r,t)}{m} \right\rangle \tag{78}$$

which states that the expectation value of velocity equals the expectation value of the mechanical momentum divided by mass.

Next, consider the momentum operator proper $\pi = \mathbf{p} - \frac{e}{c}\mathbf{a}(r,t)$, which does have explicit time dependence through $\mathbf{a}(r,t)$.

Therefore the Ehrenfest formula for π is

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \pi\rangle = \frac{i}{\hbar}\langle [H,\pi]\rangle + \left\langle \frac{\partial \pi}{\partial t} \right\rangle. \tag{79}$$

The canonical momentum operator $p = -i\hbar\nabla$ has no explicit time dependence, so the contribution of the last term of (79) is given by

$$\frac{\partial \pi}{\partial t} = -\frac{e}{c}\frac{\partial \mathbf{a}(r,t)}{\partial t} \Rightarrow \left\langle \frac{\partial \pi}{\partial t} \right\rangle = -\frac{e}{c}\left\langle \frac{\partial \mathbf{a}}{\partial t} \right\rangle. \tag{80}$$

Considering from (70) that $H = \frac{1}{2m}\sum_j \pi_j^2$, then

$$[H, \pi_k] = \frac{1}{2m}\sum_j \left[\pi_j^2, \pi_k\right] \tag{81}$$

so $[\pi_i, \pi_j]$ must be computed in order to subsequently compute $\left[\pi_j^2, \pi_k\right]$. Thus

$$[\pi_i, \pi_j] = \pi_i\pi_j - \pi_j\pi_i \tag{82}$$

Expanding $\pi_i\pi_j$ obtains

$$\pi_i\pi_j = \left(\mathbf{p}_i - \frac{e}{c}\mathbf{a}_i\right)\left(\mathbf{p}_j - \frac{e}{c}\mathbf{a}_j\right) \tag{83}$$

$$= \mathbf{p}_i\mathbf{p}_j - \frac{e}{c}(\mathbf{p}_i\mathbf{a}_j + \mathbf{a}_i\mathbf{p}_j) + \frac{e^2}{c^2}\mathbf{a}_i\mathbf{a}_j. \tag{84}$$

Similarly

$$\pi_j\pi_i = \mathbf{p}_j\mathbf{p}_i - \frac{e}{c}(\mathbf{p}_j\mathbf{a}_i + \mathbf{a}_j\mathbf{p}_i) + \frac{e^2}{c^2}\mathbf{a}_j\mathbf{a}_i. \tag{85}$$

Subtracting (85) from (84) per (82) yields

$$[\pi_i, \pi_j] = \mathbf{p}_i\mathbf{p}_j - \mathbf{p}_j\mathbf{p}_i \tag{86}$$

$$-\frac{e}{c}(\mathbf{p}_i\mathbf{a}_j - \mathbf{p}_j\mathbf{a}_i) - \frac{e}{c}(\mathbf{a}_i\mathbf{p}_j - \mathbf{a}_j\mathbf{p}_i) \tag{87}$$

$$+\frac{e^2}{c^2}(\mathbf{a}_i\mathbf{a}_j - \mathbf{a}_j\mathbf{a}_i) \tag{88}$$

Since canonical momenta commute with each other, (86) vanishes. Furthermore, since multiplication operators commute, (88) also vanishes. Thus

$$[\pi_i, \pi_j] = -\frac{e}{c}(\mathbf{p}_i\mathbf{a}_j - \mathbf{p}_j\mathbf{a}_i) - \frac{e}{c}(\mathbf{a}_i\mathbf{p}_j - \mathbf{a}_j\mathbf{p}_i). \tag{89}$$

For any sufficiently smooth function $f(\mathbf{r})$,

$$[\mathbf{p}_k, f(\mathbf{r})] = -i\hbar\frac{\partial f}{\partial x_k} \tag{90}$$

and since $\mathbf{p}_k = -i\hbar\partial_k$, therefore

$$\mathbf{p}_i\mathbf{a}_j = \mathbf{a}_j\mathbf{p}_i + [\mathbf{p}_i, \mathbf{a}_j] = \mathbf{a}_j\mathbf{p}_i - i\hbar\frac{\partial \mathbf{a}_j}{\partial x_i} \tag{91}$$

and similarly

$$\mathbf{p}_j\mathbf{a}_i = \mathbf{a}_i\mathbf{p}_j + \left[\mathbf{p}_j, \mathbf{a}_i\right] = \mathbf{a}_i\mathbf{p}_j - i\hbar\frac{\partial \mathbf{a}_i}{\partial x_j}. \tag{92}$$

Hence, the left quantity in parentheses of (87) becomes

$$\begin{aligned}\mathbf{p}_i\mathbf{a}_j - \mathbf{p}_j\mathbf{a}_i &= \left(\mathrm{a}_j\mathbf{p}_i - i\hbar\frac{\partial \mathbf{a}_j}{\partial x_i}\right) - \left(\mathbf{a}_i\mathbf{p}_j - i\hbar\frac{\partial \mathbf{a}_i}{\partial x_j}\right)\\ &= \mathbf{a}_j\mathbf{p}_i - \mathbf{a}_i\mathbf{p}_j + i\hbar\left(\frac{\partial \mathbf{a}_i}{\partial x_j} - \frac{\partial \mathbf{a}_j}{\partial x_i}\right)\end{aligned} \tag{93}$$

Plugging (93) back into $[\pi_i, \pi_j]$ yields

$$\begin{aligned}[\pi_i, \pi_j] &= -\frac{e}{c}(\mathbf{a}_j\mathbf{p}_i - \mathbf{a}_i\mathbf{p}_j + i\hbar(\partial_j\mathbf{a}_i - \partial_i\mathbf{a}_j)) - \frac{e}{c}(\mathbf{a}_i\mathbf{p}_j - \mathbf{a}_j\mathbf{p}_i)\\ &= -\frac{e}{c}\left(i\hbar\left(\frac{\partial \mathbf{a}_i}{\partial x_j} - \frac{\partial \mathbf{a}_j}{\partial x_i}\right)\right)\\ &= \frac{ie\hbar}{c}\left(\frac{\partial \mathbf{a}_i}{\partial x_j} - \frac{\partial \mathbf{a}_j}{\partial x_i}\right).\end{aligned} \tag{94}$$

Recalling the definition of curl from (24) and re-writing the indices from its previously given formulation $l \to i$ and $m \to j$ results in

$$\mathcal{H}_k = (\nabla \times \mathbf{a})_k = \sum_{i,j} \epsilon_{kij} \frac{\partial \mathbf{a}_j}{\partial x_i}. \tag{95}$$

Therefore

$$\frac{\partial \mathbf{a}_j}{\partial x_i} - \frac{\partial \mathbf{a}_i}{\partial x_j} = \epsilon_{ijk} \mathcal{H}_k \tag{96}$$

and

$$[\pi_i, \pi_j] = \frac{ie\hbar}{c} \epsilon_{ijk} \mathcal{B}_k. \tag{97}$$

Applying the identity $[AB, C] = A[B, C] + [A, C]B$ allows $\left[\pi_j^2, \pi_k\right]$ to be computed, namely

$$\begin{aligned}
\left[\pi_j^2, \pi_k\right] &= \pi_j [\pi_j, \pi_k] + [\pi_j, \pi_k] \pi_j \\
&= \pi_j [\pi_j, \pi_k] + \pi_j [\pi_j, \pi_k] - \pi_j [\pi_j, \pi_k] + [\pi_j, \pi_k] \pi_j \\
&= 2\pi_j [\pi_j, \pi_k] - (\pi_j [\pi_j, \pi_k] - [\pi_j, \pi_k] \pi_j) \\
&= 2\pi_j [\pi_j, \pi_k] - [\pi_j, [\pi_j, \pi_k]]
\end{aligned} \tag{98}$$

Continuing from (81) with the results from (97) and (98) yields

$$\begin{aligned}
[H, \pi_k] = \frac{1}{2m} \sum_j \left[\pi_j^2, \pi_k\right] &= \frac{1}{m} \sum_j \pi_j [\pi_j, \pi_k] - \frac{1}{2m} \sum_j [\pi_j, [\pi_j, \pi_k]] \\
&= \frac{ie\hbar}{cm} \sum_{j,l} \pi_j \epsilon_{jkl} \mathcal{B}_l - \frac{1}{2m} \sum_j [\pi_j, [\pi_j, \pi_k]] \\
&= \frac{ie\hbar}{cm} (\pi \times \mathcal{B})_k - \frac{1}{2m} \sum_j [\pi_j, [\pi_j, \pi_k]] .
\end{aligned} \tag{99}$$

Next, $[\pi_j, [\pi_j, \pi_k]]$ will be considered. Similar to (90),

$$[\pi_j, f(\mathbf{r})] = -i\hbar \frac{\partial f}{\partial x_j} \quad \text{for } f = \mathcal{B}_l(\mathbf{r}). \tag{100}$$

Therefore the double commutator is

$$[\pi_j, [\pi_j, \pi_k]] = \frac{ie\hbar}{c} \epsilon_{jkl} [\pi_j, \mathcal{B}_l] = \frac{ie\hbar}{c} \epsilon_{jkl} (-i\hbar) \frac{\partial \mathcal{B}_l}{\partial x_j} = \frac{e\hbar^2}{c} \epsilon_{jkl} \partial_j \mathcal{B}_l. \tag{101}$$

When the expectation value is taken $\langle [H, \pi_k] \rangle$, (101) contributes a term that is proportional to $\hbar^2$. In the classical limit $\hbar \to 0$ or when the wave packet is sufficiently localized (i.e., classical behavior of expectation values), then the term (101) vanishes. Furthermore, since this term involves derivatives of $\mathcal{B}$, in uniform magnetic fields (i.e., $\nabla \mathcal{B} = 0$), this term is exactly zero. Hence,

$$[H, \pi_k] \approx \frac{ie\hbar}{cm}(\pi \times \mathcal{B})_k. \tag{102}$$

Then, $i\hbar\langle [H, \pi_k] \rangle$ computes to

$$i\hbar\langle [H, \pi_k] \rangle \approx \frac{i}{\hbar} \cdot \frac{ie\hbar}{cm}\langle (\pi \times \mathcal{B})_k \rangle = \frac{e}{c}\left\langle \left(\frac{\pi}{m} \times \mathcal{B}\right)_k \right\rangle .) \tag{103}$$

Inserting (80) and (103) into 79) yields

$$\frac{\mathrm{d}\langle \pi \rangle}{\mathrm{d}t} = \frac{e}{c}\left\langle \frac{\pi}{m} \times \mathcal{B} \right\rangle - \frac{e}{c}\left\langle \frac{\partial \mathbf{a}}{\partial t} \right\rangle . \tag{104}$$

Since $\mathcal{E} = -\frac{\partial \mathbf{a}}{\partial t}$, $\frac{e}{c}\mathbf{v} \times \mathcal{B}$ where $\mathbf{v} = \frac{\pi}{m}$, $m\frac{\mathrm{d}\langle v \rangle}{\mathrm{d}t} = \frac{\mathrm{d}\langle \pi \rangle}{\mathrm{d}t}$, and $\langle \mathbf{v} \rangle = \frac{\mathrm{d}\langle \mathbf{r} \rangle}{\mathrm{d}t}$ then finally

$$m\frac{\mathrm{d}^2\langle \mathbf{r} \rangle}{\mathrm{d}t^2} = \left\langle e\left(\mathcal{E} + \frac{\mathbf{v}}{c} \times \mathcal{B}\right) \right\rangle \tag{105}$$

which is exactly Newton's second law with the classical Lorentz force at the level of expectation values.

5 Gauge Invariance

Next, it will be assessed whether the physical results change when the potentials in question here undergo a gauge transformation.

Recall that a gauge transformation in this specific context amounts roughly to a transformation of the electric and magnetic potentials that leaves the respective fields unchanged.

Such local transformations preserve the dynamics of the system and can be useful for assessing potentials that are non-uniquely defined in terms of the fields.

It is expected that the potentials of the foregoing quantum-mechanical Hamiltonian under a gauge transformation will not result in any physical results changing.

If this were not the case, it would contradict the result that certain physical quantities involved in the equations of motion in the classical limit are unchanged under such a transformation.

Canonical momentum $\mathbf{p} = m\mathbf{v} + \dfrac{e}{c}\mathbf{a}$ is not one such quantity as it depends on the choice of gauge.

The only physically significant quantities are those which are gauge invariant.

In this case, mechanical velocity is the gauge invariant quantity, which will now be shown to be invariant to a "classical" gauge transformation.

For the physical velocity $\pi/m = \dfrac{1}{m}\left(\mathbf{p} - \frac{e}{c}\mathbf{a}\right)$, this gauge transformation parameterized by an arbitrary scalar function $\chi(\mathbf{r}, t)$ is given by

$$\mathbf{a}'(\mathbf{r}, t) = \mathbf{a}(\mathbf{r}, t) + \nabla\chi(\mathbf{r}, t) \tag{106}$$

$$\phi'(\mathbf{r}, t) = \phi(\mathbf{r}, t) - \frac{1}{c}\frac{\partial\chi}{\partial t} \tag{107}$$

which leaves the physical fields $\mathcal{E}$ and $\mathcal{B}$ unchanged.

The Lagrangian for the charged particle is given by

$$L = \frac{1}{2}m\mathbf{v}^2 + \frac{e}{c}\mathbf{v}\cdot\mathbf{a} - e\phi. \tag{108}$$

Under the gauge transformation, the new Lagrangian L' differs from L by a total derivative

$$L' = L + \frac{e}{c}\frac{\mathrm{d}\chi}{\mathrm{d}t} \quad \text{where } \frac{\mathrm{d}\chi}{\mathrm{d}t} = \frac{\partial\chi}{\partial t} + \mathbf{v}\cdot\nabla\chi. \tag{109}$$

For canonical momentum $\mathbf{p} = \dfrac{\partial L}{\partial \mathbf{v}}$, the new canonical momentum is

$$\mathbf{p}' = \frac{\partial L'}{\partial \mathbf{v}} = \frac{\partial L}{\partial \mathbf{v}} + \frac{e}{c}\frac{\partial}{\partial \mathbf{v}}(\mathbf{v}\cdot\nabla\chi) = \mathbf{p} + \frac{e}{c}\nabla\chi. \tag{110}$$

Note that canonical momentum can be loosely considered as momentum in a particular coordinate system, and changing gauge is like changing coordinates.

The canonical momentum adjusts by $+\frac{e}{c}\nabla\chi$, but the "true" momentum relative to the new coordinates remains the same.

The mechanical momentum in the new gauge is thus computed as

$$\begin{aligned}\mathbf{p}' - \frac{e}{c}\mathbf{a}' &= \left(\mathbf{p} + \frac{e}{c}\nabla\chi\right) - \frac{e}{c}(\mathbf{a} + \nabla\chi) \\ &= \mathbf{p} + \frac{e}{c}\nabla\chi - \frac{e}{c}\mathbf{a} - \frac{e}{c}\nabla\chi \\ \Rightarrow \mathbf{p}' - \frac{e}{c}\mathbf{a}' &= \mathbf{p} - \frac{e}{c}\mathbf{a}. \end{aligned} \tag{111}$$

Therefore, the velocity itself

$$\mathbf{v} = \frac{1}{m}\left(\mathbf{p} - \frac{e}{c}\mathbf{a}\right) = \frac{1}{m}\left(\mathbf{p}' - \frac{e}{c}\mathbf{a}'\right) \tag{112}$$

is the same in both gauges.

This is reasonable in that velocity is a physically observable quantity and does not depend on the choice of gauge.

However, in quantum theory, velocity is an inherently tenuous concept.

In short, this is because of not only the broader implications of the uncertainty principle and complementarity, but also that in a very accurate description the concept of a continuous trajectory does not apply to the motion of real particles.

As such, average velocity is a pervasively more substantial concept as the average of the operator $\frac{1}{m}\left(\mathbf{p} - \frac{e}{c} - \mathbf{a}\right)$.

This operator, as in the case of zero vector potential, can be defined only when the position of the electron is not too well defined.

To further illustrate the property of gauge invariance of physically significant quantities, write the complete Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla - \frac{e}{c}\mathbf{a}\right)^2\psi + (e\phi + V)\psi. \tag{113}$$

Applying a gauge transformation to (113) yields

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla + \frac{e}{c}\nabla f - \frac{e}{c}\mathbf{a}\right)^2\psi + (e\phi' + V)\psi + \frac{e}{c}\frac{\partial f}{\partial t}\psi. \tag{114}$$

Introducing a new wave function $\psi' = e^{ief/\hbar}\psi$ and writing the new potentials as $\mathbf{a}' = \mathbf{a} + \nabla f$ and $\phi' = \phi - \frac{1}{c}\frac{\partial f}{\partial t}$ obtains that (114) is equivalent to

$$i\hbar\frac{\partial}{\partial t}(e^{ief/\hbar}\psi) = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla - \frac{e}{c}\mathbf{a}'\right)^2(e^{ief/\hbar}\psi) + (e\phi' + V)(e^{ief/\hbar}\psi). \tag{115}$$

The new wave function ψ' satisfies the same wave equation as was satisfied formerly by ψ itself, and the new wave function is therefore a new solution.

To see that the probability is the same with the new function as with the old, notice that the probability density associated with ψ' is

$$P' = |\psi'|^2 = |e^{ief/\hbar}\psi|^2 = |e^{ief/\hbar}|^2|\psi|^2. \tag{116}$$

Since $|e^{i\theta}| = 1$ for any real θ,

$$P' = |\psi|^2 = P \tag{117}$$

and thus the probability density is unchanged under the combined gauge transformation of the potentials and the new wave function.

It will now be shown that the probability current is the same expression in terms of ψ' and $\mathbf{a}'$ as it is in terms of ψ and $\mathbf{a}$.

Let $\alpha = ef/\hbar$, which is a real function, so that it may be written $\psi' = e^{i\alpha}\psi$. Then

$$\psi'^{\star} = e^{-i\alpha}\psi^{\star}. \tag{118}$$

The gradient of ψ' is computed as

$$\nabla\psi' = \nabla(e^{i\alpha}\psi) = e^{i\alpha}\nabla\psi + i(\nabla\alpha)e^{i\alpha}\psi = e^{i\alpha}\left(\nabla\psi + i\frac{e}{\hbar}(\nabla f)\psi\right). \tag{119}$$

Similarly,

$$\nabla\psi'^{\star} = e^{-i\alpha}\left(\nabla\psi^{\star} - i\frac{e}{\hbar}(\nabla f)\psi^{\star}\right). \tag{120}$$

Following (66) and (67), the combinations below which appear in the probability current are calculated as

$$\psi'^{\star}\nabla\psi' = e^{-i\alpha}\psi^{\star}\cdot e^{i\alpha}\left(\nabla\psi + i\frac{e}{\hbar}\nabla f\psi\right) = \psi^{\star}\left(\nabla\psi + i\frac{e}{\hbar}\nabla f\psi\right), \tag{121}$$

$$\psi'\nabla\psi'^{\star} = e^{i\alpha}\psi\cdot e^{-i\alpha}\left(\nabla\psi^{\star} - i\frac{e}{\hbar}\nabla f\psi^{\star}\right) = \psi\left(\nabla\psi^{\star} - i\frac{e}{\hbar}\nabla f\psi^{\star}\right). \tag{122}$$

Subtracting (122) from (121) obtains

$$\begin{aligned}\psi'^{\star}\nabla\psi' - \psi'\nabla\psi'^{\star} &= \psi^{\star}\nabla\psi + i\frac{e}{\hbar}\psi^{\star}(\nabla f)\psi - \psi\nabla\psi^{\star} + i\frac{e}{\hbar}\psi(\nabla f)\psi^{\star}\\ &= (\psi^{\star}\nabla\psi - \psi\nabla\psi^{\star}) + i\frac{e}{\hbar}(\nabla f)(\psi^{\star}\psi + \psi\psi^{\star})\\ &= (\psi^{\star}\nabla\psi - \psi\nabla\psi^{\star}) + 2i\frac{e}{\hbar}(\nabla f)|\psi|^2. \end{aligned} \tag{123}$$

Multiplying (123) through by the pre-factor $\frac{\hbar}{2mi}$ results in

$$\frac{\hbar}{2mi}\left(\psi'^{\star}\nabla\psi' - \psi'\nabla\psi'^{\star}\right) = \frac{\hbar}{2mi}\left(\psi^{\star}\nabla\psi - \psi\nabla\psi^{\star}\right) + \frac{e}{m}(\nabla f)|\psi|^2. \tag{124}$$

Following from the second (gauge) term on the right hand side of (67) is computed as

$$-\frac{e}{mc}\mathbf{a}|\psi|^2 \Rightarrow -\frac{e}{mc}\mathbf{a}'|\psi'|^2 = -\frac{e}{mc}(\mathbf{a} + \nabla f)|\psi|^2 = -\frac{e}{mc}\mathbf{a}|\psi|^2 - \frac{e}{mc}(\nabla f)|\psi|^2. \tag{125}$$

Adding (124) and (125) results in

$$\begin{aligned}\mathbf{S}' &= \frac{\hbar}{2mi}\left(\psi^{\star}\nabla\psi - \psi\nabla\psi^{\star}\right) - \frac{e}{mc}\mathbf{a}|\psi|^2 + \frac{e}{m}(\nabla f)|\psi|^2 - \frac{e}{mc}(\nabla f)|\psi|^2\\ &= \frac{\hbar}{2mi}\left(\psi^{\star}\nabla\psi - \psi\nabla\psi^{\star}\right) - \frac{e}{mc}\mathbf{a}|\psi|^2 \end{aligned} \tag{126}$$

which is identical in form to (67).

6 Uniform Magnetic Field

It will now be shown that the following choice of vector potential does not lead to a uniform magnetic field $\mathcal{B}$ directed in the z-direction:

$$a_x = \frac{\mathcal{B}y}{2}, \quad a_y = \frac{\mathcal{B}z}{2}, \quad a_z = 0. \tag{127}$$

The components of the curl $\mathcal{B} = \nabla \times \mathbf{a}$ will be calculated given (127).

$$\mathcal{B}_x = \frac{\partial a_z}{\partial y} - \frac{\partial a_y}{\partial z} = 0 - \frac{\partial}{\partial z}\left(\frac{\mathcal{B}z}{2}\right) = -\frac{\mathcal{B}}{2} \tag{128}$$

$$\mathcal{B}_y = \frac{\partial a_x}{\partial z} - \frac{\partial a_z}{\partial x} = 0 - 0 = 0 \tag{129}$$

$$\mathcal{B}_z = \frac{\partial a_y}{\partial x} - \frac{\partial a_x}{\partial y} = 0 - \frac{\partial}{\partial y}\left(\frac{\mathcal{B}y}{2}\right) = -\frac{\mathcal{B}}{2} \tag{130}$$

Therefore

$$\mathcal{B} = \left(-\frac{\mathcal{B}}{2}, 0, -\frac{\mathcal{B}}{2}\right) \tag{131}$$

which is not a uniform field purely in the z-direction.

However, the following choice of vector potential

$$a_x = -\frac{\mathcal{B}y}{2}, \quad a_y = \frac{\mathcal{B}x}{2}, \quad a_z = 0. \tag{132}$$

produces a uniform magnetic field in the z-direction, which can be seen by calculating

$$\mathcal{B}_x = \frac{\partial a_z}{\partial y} - \frac{\partial a_y}{\partial z} = 0 - 0 = 0 \tag{133}$$

$$\mathcal{B}_y = \frac{\partial a_x}{\partial z} - \frac{\partial a_z}{\partial x} = 0 - 0 = 0 \tag{134}$$

$$\mathcal{B}_z = \frac{\partial a_y}{\partial x} - \frac{\partial a_x}{\partial y} = \frac{\partial}{\partial x}\left(\frac{\mathcal{B}x}{2}\right) - \frac{\partial}{\partial y}\left(-\frac{\mathcal{B}y}{2}\right) = \frac{\mathcal{B}}{2} + \frac{\mathcal{B}}{2} = \mathcal{B}. \tag{135}$$

Therefore $\mathcal{B} = (0, 0, \mathcal{B})$ which indeed is a uniform magnetic field in the z-direction.

Next, consider the potentials

$$a_x = -\mathcal{B}y, \quad a_y = a_z = 0. \tag{136}$$

By calculating the components of the curl

$$\mathcal{B}_x = \frac{\partial a_z}{\partial y} - \frac{\partial a_y}{\partial z} = 0 - 0 = 0 \tag{137}$$

$$\mathcal{B}_y = \frac{\partial a_x}{\partial z} - \frac{\partial a_z}{\partial x} = 0 - 0 = 0 \tag{138}$$

$$\mathcal{B}_z = \frac{\partial a_y}{\partial x} - \frac{\partial a_x}{\partial y} = 0 - \frac{\partial}{\partial y}(-\mathcal{B}y) = \mathcal{B} \tag{139}$$

the resulting field is thus $\mathcal{B} = (0, 0, \mathcal{B})$.

Denote the potential whose components are given in (132) as $\mathbf{a}^S$ and denote the potential whose components are given in (136) as $\mathbf{a}^L$.

To see that these potentials are related by a gauge transformation, a scalar function $f(\mathbf{r})$ is sought such that

$$\mathbf{a}^S = \mathbf{a}^L + \nabla f. \tag{140}$$

Next, compute

$$\nabla f = \mathbf{a}^S - \mathbf{a}^L = \left(-\frac{\mathcal{B}y}{2} + \mathcal{B}y, \frac{\mathcal{B}x}{2} - 0, 0\right) = \left(\frac{\mathcal{B}y}{2}, \frac{\mathcal{B}x}{2}, 0\right). \tag{141}$$

Integrating the x-component of (141) yields

$$\frac{\partial f}{\partial x} = \frac{\mathcal{B}y}{2} \Rightarrow \int \partial f = \int \frac{\mathcal{B}y}{2} \partial x \Rightarrow f = \frac{\mathcal{B}}{2}xy + g(y, z) \tag{142}$$

Since the y-component of (141) is $\frac{\partial f}{\partial y} = \frac{\mathcal{B}x}{2}$, the function $f = \frac{\mathcal{B}}{2}xy + g(y, z)$ is satisfied by $g(y, z) = 0$. Thus, the gauge function is

$$f(x, y) = \frac{\mathcal{B}}{2}xy. \tag{143}$$

With the potential $\mathbf{a}^S$, the Hamiltonian becomes

$$H = \frac{-\hbar^2}{2m}\nabla^2 + \frac{e\mathcal{B}}{2mc}\frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) + \frac{e^2}{8mc^2}\mathcal{B}^2(x^2+y^2) + V. \tag{144}$$

7 The Zeeman Splitting of Levels of Different Azimuthal Quantum Number m

The Hamiltonian (144) can be used to treat problems such as, for example, the Zeeman splitting of energy levels in a magnetic field.

(144) may be expressed in spherical polar coordinates as

$$H = \frac{-\hbar^2}{\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{L^2}{\hbar^2 r^2}\right) + \frac{e\mathcal{B}}{2\mu c}\frac{\hbar}{i}\frac{\partial}{\partial\phi} + \frac{e^2\mathcal{B}^2}{8\mu^2c^2}\rho^2 + V(r). \tag{145}$$

where $\rho = x^2 + y^2$ and reduced mass is being denoted by $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$.

Note that $V(r)$ is a spherically symmetric potential, which is assumed to be the type generally present in atoms.

The Hamiltonian (145) differs from a formulation of the Hamiltonian which holds in the absence of a magnetic field in two respects.

(1) There is a field proportional term, $\dfrac{e\hbar}{2\mu c}\dfrac{\hbar}{i}\dfrac{\partial}{\partial\phi}$, added to H.

(2) The effective potential is changed by the addition of $\dfrac{e^2\mathcal{B}^2}{2\mu c^2}\rho^2$.

The latter effect involves $\mathcal{B}^2$ and thus for weak fields, it produces a second-order correction that overall may be neglected.

To the first-order, then, the predominant effect of the magnetic field is to chage the Hamiltonian by $\nabla H = \dfrac{e\mathcal{B}}{2\mu c}\dfrac{\hbar}{i}\dfrac{\partial}{\partial\phi}$.

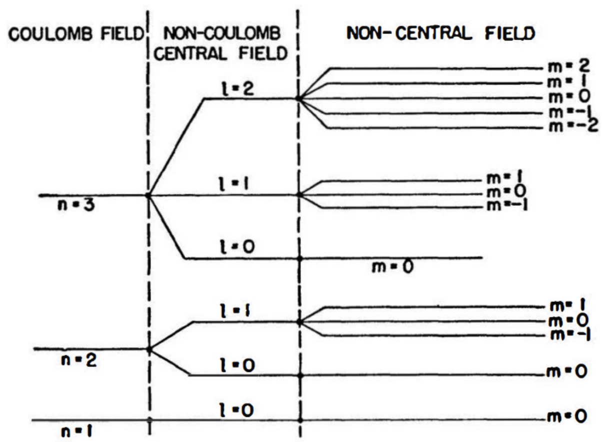
Note that in this approximation the Hamiltonian still commutes with L^2 and with L_z, so that L^2, L_z, and H can be specified simultaneously.

Assuming $L^2 = l(l+1)\hbar^2$ and $L_z = m\hbar$, where l denotes the orbital angular momentum quantum number and m denotes the azimuthal quantum number, thus obtains

$$H = \frac{-\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{l(l+1)}{r^2}\right] + \frac{e\mathcal{B}}{2\mu c}\hbar m + V(r). \tag{146}$$

The only effect of the magnetic field is then to add a constant to the energy, proportional to the azimuthal quantum number m.

Thus means that some of the degeneracy is removed because levels of different m now have different energies (see below; recall that n denotes the principal quantum number). To a first approximation, the wave functions are not



altered, since, with the neglect of the term $\frac{e^2\mathcal{B}^2}{8\mu^2c^2}\rho^2$, the radial wave equation is exactly the same as before.

The change of energy levels can be interpreted as follows.

7.1 Magnetic Moment of an Orbiting Electron (Classical)

Consider an electron of charge $-e$ and reduced mass μ moving in a closed orbit (not necessarily circular) with instantaneous velocity $\mathbf{v}$.

The orbital angular momentum is

$$L = \mu\mathbf{r} \times \mathbf{v}. \tag{147}$$

The orbiting electron constitutes a current loop, and its effective current I is the charge passing a given point per unit time

$$I = -\frac{e}{T} \tag{148}$$

where T is the period of the orbit.

The magnetic moment M of a current loop is

$$M = I \cdot \mathbf{A} \tag{149}$$

where $\mathbf{A}$ is the vector area enclosed by the orbit. For a general planar orbit,

$$\mathbf{A} = \frac{1}{2}\int (\mathbf{r} \times \mathrm{d}\mathbf{r}) = \frac{1}{2T}\int_0^T (\mathbf{r} \times \mathbf{v})\ \mathrm{d}t \cdot T = \frac{1}{2}\langle \mathbf{r} \times \mathbf{v}\rangle T. \tag{150}$$

Averaging over one period,

$$M = I \cdot \frac{1}{2}\int_0^T (\mathbf{r} \times \mathbf{v})\ \mathrm{d}t = \left(-\frac{e}{T}\right) \cdot \frac{1}{2}\langle \mathbf{r} \times \mathbf{v}\rangle T = -\frac{e}{2}\langle \mathbf{r} \times \mathbf{v}\rangle. \tag{151}$$

(147) implies

$$\langle \mathbf{r} \times \mathbf{v}\rangle = \frac{L}{\mu} \tag{152}$$

therefore

$$M = -\frac{e}{2\mu}L. \tag{153}$$

In Gaussian (cgs) units, the factor of c must be restored in the definition of the magnetic moment because the Lorentz force has v/c. The relation (153) then becomes

$$M = -\frac{e}{2\mu c}L \tag{154}$$

or for a positive charge $+e$

$$M = \frac{e}{2\mu c}L. \tag{155}$$

7.2 Bohr Magneton and Zeeman Effect

Given (155), the energy of a magnetic moment in a magnetic field $\mathcal{B}$ is

$$W = M \cdot \mathcal{B} = \frac{eL \cdot \mathcal{B}}{2\mu c} = \frac{e\mathcal{B}}{2\mu c} L_z. \tag{156}$$

since the uniform magnetic field $\mathcal{B}$ is assumed to be in the z-direction. Writing $L_z = m\hbar$ obtains

$$W = \frac{e\mathcal{B}}{2\mu c} \hbar m. \tag{157}$$

The magnetic moment of an electron with unit angular momentum $\hbar$ is called a *Bohr magneton.*

This magnetic moment is equal to $\dfrac{e\hbar}{2\mu c}$. Thus, the magnetic moment of an electron in an atom is some integral multiple of a Bohr magneton.

The foregoing derivation for the splitting of energy levels gives rise to a change in the pattern of spectral lines emitted by an atom.

This change is known as the Zeeman effect.

The quadratic term $\dfrac{e^2\mathcal{B}^2}{8\mu c^2}\rho^2$ may become important for very strong magnetic fields, where it leads to a general shifting and reordering of energy levels, which is connected with the Paschen-Back effect.

The Paschen-Back effect is a phenomenon that occurs when an external magnetic field is strong enough to decouple an atom's orbital angular momentum from its spin angular momentum.

In this strong-field regime, both momenta precess independently around the magnetic field, simplifying complex spectral line splittings.