The molecular Hamiltonian

Trygve Helgaker

Centre for Theoretical and Computational Chemistry
Department of Chemistry, University of Oslo, Norway

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The electronic Hamiltonian in an electromagnetic field

- Classical mechanics of particles
  - Newtonian mechanics (1687)
  - Lagrangian mechanics (1788)
  - Hamiltonian mechanics (1833)
- Electromagnetic fields
  - Maxwell's equations (1864)
  - scalar and vector potentials
  - gauge transformations
- Spin-free electron in an electromagnetic field
  - the Lagrangian and Hamiltonian of a particle in an electromagnetic field
  - the Schrödinger equation (1925)
- Spinning electron in an electromagnetic field
  - the Schrödinger–Pauli equation (Pauli, 1927)
  - the Dirac equation (1928)

Classical mechanics

- The motion of matter is described by Newton's equations:

$$\mathbf{F}(\mathbf{r}, \mathbf{v}, t) = m\mathbf{a}$$

  - the force defines the system and is obtained from experiment
  - conservative forces (e.g., gravitational forces) are obtained from potentials:

$$\mathbf{F}(\mathbf{r}) = -\boldsymbol{\nabla} V(\mathbf{r})$$

- Radiation is described by Maxwell's equations:

$$\begin{aligned}
\boldsymbol{\nabla} \cdot \mathbf{E} &= \rho/\varepsilon_0 && \leftarrow \text{Coulomb's law} \\
\boldsymbol{\nabla} \times \mathbf{B} - \varepsilon_0\mu_0\, \partial\mathbf{E}/\partial t &= \mu_0\mathbf{J} && \leftarrow \text{Ampère's law} \\
\boldsymbol{\nabla} \cdot \mathbf{B} &= 0 \\
\boldsymbol{\nabla} \times \mathbf{E} + \partial\mathbf{B}/\partial t &= \mathbf{0} && \leftarrow \text{Faraday's law of induction}
\end{aligned}$$

- The interaction between matter and radiation is described by the Lorentz force:

$$\mathbf{F}(\mathbf{r}, \mathbf{v}) = z(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

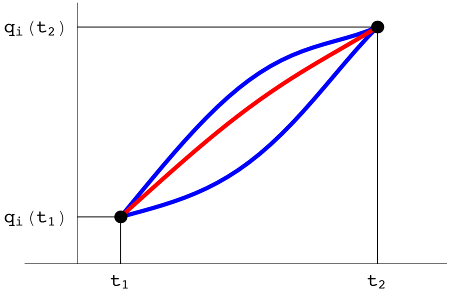
Lagrangian mechanics: the principle of least action

- For a system of n degrees of freedom, there are
  - n generalized coordinates q_i in configuration space
  - n generalized velocities $\dot{q}_i$
- The principle of least action (Hamilton's principle):

  For each system, there exists a Lagrangian $L(q_i, \dot{q}_i, t)$ such that the action integral

$$S = \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t)\, \mathrm{d}t \quad \leftarrow \quad \text{action integral}$$

  is an extremum for the trajectory taken by the system in configuration space



Lagrange's equations

- From the principle of least action, we obtain

$$\delta S = \delta \int_{t_1}^{t_2} L(q_i, \dot{q}_i, t)\,\mathrm{d}t = \int_{t_1}^{t_2} \left(\frac{\partial L}{\partial q_i}\delta q_i + \frac{\partial L}{\partial \dot{q}_i}\delta \dot{q}_i \right) \mathrm{d}t$$

$$= \int_{t_1}^{t_2} \left[\frac{\partial L}{\partial q_i}\delta q_i - \left(\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} \right) \delta q_i \right] \mathrm{d}t = 0$$

- The Lagrangian therefore satisfies the following second-order differential equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i} \qquad \leftarrow \text{Lagrange's equations of motion}$$

  - there is one such equation for each degree of freedom
- The scalar Lagrangian defines the system:
  - it is determined to reproduce the equations of motion consistent with experiment
  - Lagrange's equations preserve their form in any coordinate system
- The Lagrangian formulation is more general than the Newtonian one:
  - it provides a unified description of matter and fields
  - it represents the springboard for quantum mechanics

The arbitrariness of the Lagrangian and gauge transformations

- The Lagrangian is not uniquely defined
- Let us assume that the Lagrangian $L(q, \dot{q}, t)$ satisfies the equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}} = \frac{\partial L}{\partial q}$$

- Consider now the following transformed Lagrangian where the arbitrary gauge function $f(q, t)$ is independent of the velocity $\dot{q}$:

$$L'(q, \dot{q}, t) = L(q, \dot{q}, t) + \frac{\mathrm{d}}{\mathrm{d}t} f(q, t)$$

- This Lagrangian satisfies the same equations of motion as the old one:

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L'}{\partial \dot{q}} &= \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}} + \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial}{\partial \dot{q}}\left(\frac{\partial f}{\partial q}\dot{q} + \frac{\partial f}{\partial t}\right) \\ &= \frac{\partial L}{\partial q} + \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial f}{\partial q} = \frac{\partial}{\partial q}\left(L + \frac{\mathrm{d}f}{\mathrm{d}t}\right) = \frac{\partial L'}{\partial q} \end{aligned}$$

- This is an example of a gauge transformation

Conservative systems

- The Lagrangian of a particle in a conservative field may be written as

$$L = \underbrace{T(q, \dot{q})}_{\text{kinetic energy}} - \underbrace{V(q)}_{\text{potential energy}}$$

- The Lagrangian is thus easily set up for any conservative system, in any convenient coordinate system.
- Example: assuming a Cartesian coordinate system,

$$L = \frac{1}{2} m v^2 - V(\mathbf{r}),$$

  we find that Lagrange's equations immediately reduce to Newton's equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \mathbf{v}} = \frac{\partial L}{\partial \mathbf{r}} \quad \Rightarrow \quad \frac{\mathrm{d}}{\mathrm{d}t} m\mathbf{v} = -\boldsymbol{\nabla} V(\mathbf{r}) \quad \Rightarrow \quad m\mathbf{a} = \mathbf{F}.$$

- For particles in a (nonconservative) electromagnetic field, the Lagrangian can be cast in a similar (but slightly different) form as discussed later

Energy

- In Lagrangian mechanics, the energy function is defined as:

$$h(q, \dot{q}, t) = \frac{\partial L}{\partial \dot{q}} \dot{q} - L(q, \dot{q}, t)$$

- Example: for a conservative Cartesian system with $L = \frac{1}{2} m v^2 - V(\mathbf{r})$ we obtain:

$$h = \frac{\partial L}{\partial \mathbf{v}} \mathbf{v} - L = \frac{\partial T}{\partial \mathbf{v}} \mathbf{v} - (T - V) = 2T - T + V = T + V = \text{ total energy}$$

- h is the total energy whenever $T(\dot{q})$ is quadratic in $\dot{q}$ and $V(q)$ is independent of $\dot{q}$
- Note: the energy function h is conserved if L does not depend explicitly on time:

$$\frac{\mathrm{d}h}{\mathrm{d}t} = -\frac{\partial L}{\partial t}$$

  - proof:

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial L}{\partial \dot{q}} \dot{q} \right) - \frac{\mathrm{d}L}{\mathrm{d}t}$$

$$= \left[\left(\frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial L}{\partial \dot{q}} \right) \dot{q} + \frac{\partial L}{\partial \dot{q}} \ddot{q} \right] - \left[\frac{\partial L}{\partial q} \dot{q} + \frac{\partial L}{\partial \dot{q}} \ddot{q} + \frac{\partial L}{\partial t} \right] = -\frac{\partial L}{\partial t}$$

Generalized momentum

- The generalized momentum p_i conjugate to generalized coordinate q_i is defined as

$$p_i = \frac{\partial L}{\partial \dot{q}_i} \quad \leftarrow \text{generalized momentum conjugate to } q$$

- For a conservative system in Cartesian coordinates with Lagrangian

$$L = \frac{1}{2} m v^2 - V(\mathbf{r})$$

the conjugate momentum corresponds to the linear momentum:

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = \frac{\partial T}{\partial \mathbf{v}} = \frac{1}{2} m \frac{\partial v^2}{\partial \mathbf{v}} = m\mathbf{v} \quad \leftarrow \text{linear momentum}$$

- The momentum p_i conjugate to q_i is conserved if L does not depend on q_i:

$$\dot{p}_i = \frac{\mathrm{d}p_i}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i} = 0 \quad \leftarrow \text{if } L \text{ is independent of } q_i$$

  - such coordinates are said to be cyclic
- Compare: h is conserved if L does not depend explicitly on t,
  p_i is conserved if L does not depend explicitly on q_i

Hamiltonian mechanics

- For a system of n degrees of freedom, there are n second-order differential equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}$$

  - the motion is fully specified by the initial values of the n coordinates and n velocities
  - in this sense, we may view q_i and $\dot{q}_i$ as $2n$ independent variables

- Alternatively, let us treat q_i and p_i as $2n$ independent variables:

$$\{q_i, \dot{q}_i\} \quad \rightarrow \quad \{q_i, p_i\}$$

- Possible advantages of such a scheme:
  - first-order equations
  - better suited to cyclic coordinates

- This can be achieved by convex conjugation since:
  - L is convex in $\dot{q}$
  - p is the derivative of L with respect to $\dot{q}$:

$$p_i = \frac{\partial L}{\partial \dot{q}_i}$$

Hamiltonian mechanics

- The Lagrangian is convex in $\dot{q}$ and may be represented by its Legendre transform:

$$H(q,p,t) = \max_{\dot{q}} \left[p\dot{q} - L(q,\dot{q},t)\right] \quad \leftarrow \quad \text{Hamiltonian}$$

$$L(q,\dot{q},t) = \max_{p} \left[p\dot{q} - H(q,p,t)\right] \quad \leftarrow \quad \text{Lagrangian}$$

- The two stationary conditions establish the reciprocal relations:

$$p = \frac{\partial L}{\partial \dot{q}} \quad \leftarrow \quad \text{definition of conjugate momentum } p$$

$$\dot{q} = \frac{\partial H}{\partial p} \quad \leftarrow \quad \text{Hamilton's equation of motion for } q$$

- The equation for $\dot{p}$ is obtained from Lagrange's equation of motion

$$\dot{p} = \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}} = \frac{\partial L}{\partial q} = -\frac{\partial H}{\partial q} \quad \leftarrow \quad \text{Hamilton's equation of motion for } p$$

  where the last relation follows by differentiating the Legendre transformation
- The Hamiltonian is the energy, whose derivates are the equations of motion:

$$\boxed{\dot{p} = -\frac{\partial H}{\partial q}, \quad \dot{q} = \frac{\partial H}{\partial p}}$$

Prescription for setting up the Hamiltonian

1. Choose n generalized coordinates q_i
2. Set up the Lagrangian $L\left(q_i, \dot{q}_i, t\right)$ such that

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i} \tag{1}$$

   reproduces the equations of motion.

3. Introduce the conjugate momenta

$$p_i = \frac{\partial L}{\partial \dot{q}_i}. \tag{2}$$

4. Construct the Hamiltonian:

$$H = \sum_i p_i \dot{q}_i - L\left(q_i, \dot{q}_i, t\right) \tag{3}$$

   and invert (**??**) to express the Hamiltonian $H\left(q_i, p_i\right)$ in terms of q_i and p_i.

5. Write down Hamilton's equations of motion:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}. \tag{4}$$

Comparison of Lagrangian and Hamiltonian mechanics

Lagrangian mechanics	Hamiltonian mechanics
n second-order equations: $\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}$	$2n$ first-order equations: $\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$
q_i are the primary variables in configuration space, $\dot{q}_i$ secondary variables	q_i and p_i are independent variables in phase space, connected only by the equations of motion
the state of the system is determined when the variables $(q_i, \dot{q}_i)$ are known at a given time t	the state of the system is defined by a point (q_i, p_i) in phase space, moving on a trajectory that satisfies Hamilton's equations of motion

Poisson brackets

- The Poisson bracket of two dynamical variables $A(q, p, t)$ and $B(q, p, t)$ is

$$\{A, B\} = \sum_i \left(\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial q_i} \frac{\partial A}{\partial p_i} \right)$$

- The fundamental Poisson brackets among conjugate coordinates and momenta are:

$$\{q_i, q_j\} = 0, \quad \{p_i, p_j\} = 0, \quad \{q_i, p_j\} = \delta_{ij}$$

- The total time derivatives are given by

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{\partial A}{\partial q}\dot{q} + \frac{\partial A}{\partial p}\dot{p} + \frac{\partial A}{\partial t} = \frac{\partial A}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial A}{\partial p}\frac{\partial H}{\partial q} + \frac{\partial A}{\partial t}$$

  and may therefore be expressed compactly as

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \{A, H\} + \frac{\partial A}{\partial t}$$

- The equations of motion:

$$\dot{q} = \{q, H\}, \quad \dot{p} = \{p, H\}, \quad \frac{\mathrm{d}H}{\mathrm{d}t} = \frac{\partial H}{\partial t}$$

Quantization of a particle in conservative force field

- The Hamiltonian formulation is more general than the Newtonian formulation:
  - it is invariant to coordinate transformations
  - it provides a uniform description of matter and radiation
  - it constitutes the springboard to quantum mechanics
- The Hamiltonian function (the total energy) of a particle in a conservative force field:

$$H(q,p) = \frac{p^2}{2m} + V(q)$$

- Standard rule for quantization (in Cartesian coordinates):
  - perform the substitutions

$$\mathbf{p} \to -\mathrm{i}\hbar\boldsymbol{\nabla}, \quad H \to \mathrm{i}\hbar\frac{\partial}{\partial t}$$

  - multiply the resulting expression by the wave function $\Psi(q)$ from the right:

$$\mathrm{i}\hbar\frac{\partial\Psi(q)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(q)\right]\Psi(q)$$

- This approach is sufficient for a treatment of electrons in an electrostatic field
- It is insufficient for nonconservative systems, in a general electromagnetic field.

Review: Hamiltonian mechanics

- A system of particles is described by their positions q_i and conjugate momenta p_i
- For each system, a Hamiltonian $H(q_i, p_i)$ exists with the equations of motion:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \text{(Hamilton's equations of motion)}$$

- Example: a single particle of mass m in a conservative force field $F(q)$
  - the Hamiltonian function is constructed from a scalar potential:

$$H(q, p) = \frac{p^2}{2m} + V(q), \quad F(q) = -\frac{\partial V(q)}{\partial q}$$

  - Hamilton's equations are equivalent to Newton's equation:

$$\left.\begin{aligned} \dot{q} &= \tfrac{\partial H(q,p)}{\partial p} = \tfrac{p}{m} \\ \dot{p} &= -\tfrac{\partial H(q,p)}{\partial q} = -\tfrac{\partial V(q)}{\partial q} \end{aligned}\right\} \Rightarrow m\ddot{q} = F(q) \quad \text{(Newton's equation of motion)}$$

- Newton's equations are second order, Hamilton's equations are first order
- We must now generalize this approach to particles in an electromagnetic field

The Lorentz force and Maxwell's equations

- In the presence of an electric field **E** and a magnetic field (magnetic induction) **B**, a classical particle of charge z experiences the Lorentz force:

$$\mathbf{F} = z\,(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

  - since this force depends on the velocity **v** of the particle, it is not conservative

- The electric and magnetic fields **E** and **B** satisfy Maxwell's equations:

$$\begin{aligned} \boldsymbol{\nabla} \cdot \mathbf{E} &= \rho/\varepsilon_0 && \leftarrow \text{Coulomb's law} \\ \boldsymbol{\nabla} \times \mathbf{B} - \varepsilon_0\mu_0\, \partial \mathbf{E}/\partial t &= \mu_0 \mathbf{J} && \leftarrow \text{Ampère's law with Maxwell's correction} \\ \boldsymbol{\nabla} \cdot \mathbf{B} &= 0 && \\ \boldsymbol{\nabla} \times \mathbf{E} + \partial \mathbf{B}/\partial t &= \mathbf{0} && \leftarrow \text{Faraday's law of induction} \end{aligned}$$

  - when the charge and current densities $\rho(\mathbf{r}, t)$ and $\mathbf{J}(\mathbf{r}, t)$ are known, Maxwell's equations can be solved for $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$
  - on the other hand, since the charges (particles) are driven by the Lorentz force, $\rho(\mathbf{r}, t)$ and $\mathbf{J}(\mathbf{r}, t)$ are functions of $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$

- We shall consider the motion of particles in a given (fixed) electromagnetic field

Scalar and vector potentials

- The second, homogeneous pair of Maxwell's equations involve only **E** and **B**:

$$\nabla \cdot \mathbf{B} = 0 \tag{1}$$

$$\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0} \tag{2}$$

1. Equation (**??**) is satisfied by introducing the vector potential **A**:

$$\nabla \cdot \mathbf{B} = 0 \quad \Rightarrow \quad \mathbf{B} = \nabla \times \mathbf{A} \qquad \leftarrow \text{vector potential} \tag{3}$$

2. Inserting Eq. (**??**) in Eq. (**??**) and introducing the scalar potential ϕ, we obtain

$$\nabla \times \left(\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} \right) = \mathbf{0} \quad \Rightarrow \quad \mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} = -\nabla \phi \qquad \leftarrow \text{scalar potential}$$

- The second pair of Maxwell's equations are thus automatically satisfied by writing

$$\mathbf{E} = -\nabla \phi - \frac{\partial \mathbf{A}}{\partial t}$$

$$\mathbf{B} = \nabla \times \mathbf{A}$$

- The potentials $(\phi, \mathbf{A})$ contain four rather than six components as in $(\mathbf{E}, \mathbf{B})$
- They are obtained by solving the first, inhomogeneous pair of Maxwell's equations, which contains ρ and **J**

Gauge transformations

- The scalar and vector potentials ϕ and $\mathbf{A}$ are not unique
- Consider the following transformation of the potentials:

$$\left.\begin{array}{l}\phi' = \phi - \frac{\partial f}{\partial t} \\ \mathbf{A}' = \mathbf{A} + \boldsymbol{\nabla} f\end{array}\right\} f = f(q,t) \quad \leftarrow \text{gauge function of position and time}$$

- This gauge transformation of the potentials does not affect the physical fields:

$$\mathbf{E}' = -\boldsymbol{\nabla}\phi' - \frac{\partial \mathbf{A}'}{\partial t} = -\boldsymbol{\nabla}\phi + \boldsymbol{\nabla}\frac{\partial f}{\partial t} - \frac{\partial \mathbf{A}}{\partial t} - \frac{\partial \boldsymbol{\nabla} f}{\partial t} = \mathbf{E}$$

$$\mathbf{B}' = \boldsymbol{\nabla} \times (\mathbf{A} + \boldsymbol{\nabla} f) = \mathbf{B} + \boldsymbol{\nabla} \times \boldsymbol{\nabla} f = \mathbf{B}$$

- We are free to choose $f(q,t)$ so as to make ϕ and $\mathbf{A}$ satisfy additional conditions.
- In the Coulomb gauge, the gauge function is chosen such that the vector potential becomes divergenceless:

$$\boldsymbol{\nabla} \cdot \mathbf{A} = 0 \quad \leftarrow \text{Coulomb gauge}$$

- In the following, we shall assume the Coulomb gauge (without loss of generality)

Particle in an electromagnetic field

- For a particle in an electromagnetic field, we must set up a Lagrangian such that

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}$$

reduces to Newton's equations with the Lorentz force

$$\mathbf{F} = z\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right), \quad \mathbf{E} = -\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$$

- This is not a conservative system, for which

$$L = T - V, \quad F_i = -\frac{\partial V}{\partial q_i}$$

- Rather, it belongs to a broader class of systems, for which

$$L = T - U, \quad F_i = -\frac{\partial U}{\partial q_i} + \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial U}{\partial \dot{q}_i}\right)$$

- For a particle subject to the Lorentz force, the generalized potential U is given by

$$U = z\left(\phi - \mathbf{v} \cdot \mathbf{A}\right) \quad \leftarrow \text{velocity-dependent potential}$$

and the Lagrangian becomes

$$L = T - z\left(\phi - \mathbf{v} \cdot \mathbf{A}\right) \quad \leftarrow \text{particle in an electromagnetic field}$$

Conjugate momentum in an electromagnetic field

- We recall that, for a conservative system described by Lagrangian of the form

$$L(q, \dot{q}) = T(\dot{q}) - V(q),$$

the conjugate momentum in Cartesian coordinates

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = \frac{\partial T}{\partial \mathbf{v}} = m\mathbf{v} \equiv \boldsymbol{\pi}$$

is equal to the linear (kinetic) momentum $\boldsymbol{\pi}$:

$$\mathbf{p} = \boldsymbol{\pi} \quad \leftarrow \text{particle in a conservative field}$$

- By contrast, for a nonconservative system described by Lagrangian

$$L(q, \dot{q}) = T(\dot{q}) - U(q, \dot{q}),$$

the conjugate and kinetic momenta are different

- In particular, for a particle in an electromagnetic field

$$L = T - z(\phi - \mathbf{v} \cdot \mathbf{A})$$

we obtain the following conjugate momentum:

$$\mathbf{p} = \frac{\partial L}{\partial \mathbf{v}} = \frac{\partial T}{\partial \mathbf{v}} + z\mathbf{A} \quad \Rightarrow \quad \mathbf{p} = \boldsymbol{\pi} + z\mathbf{A}$$

The Hamiltonian in an electromagnetic field

- We recall that, for a conservative system with Lagrangian

$$L = T(\dot{q}) - V(q),$$

where $T(\dot{q})$ is quadratic in $\dot{q}$, the Hamiltonian is given by

$$H = T(\dot{q}) + V(q).$$

- Let us now consider the nonconservative system consisting of a particle in a field

$$L = T(\dot{q}) - U(q, \dot{q}) = \frac{1}{2}mv^2 - z(\phi - \mathbf{v} \cdot \mathbf{A}).$$

- From the conjugate momentum

$$\mathbf{p} = m\mathbf{v} + z\mathbf{A},$$

we obtain the Hamiltonian

$$H = \mathbf{p} \cdot \mathbf{v} - L = \left(mv^2 + z\mathbf{v} \cdot \mathbf{A}\right) - \left(\frac{1}{2}mv^2 - z\phi + z\mathbf{v} \cdot \mathbf{A}\right) = \frac{1}{2}mv^2 + z\phi = T + z\phi.$$

- Expressed in canonical coordinates, the Hamiltonian now becomes:

$$H = T + z\phi = \frac{(\mathbf{p} - z\mathbf{A}) \cdot (\mathbf{p} - z\mathbf{A})}{2m} + z\phi$$

Quantization of a particle in an electromagnetic field

- We have constructed a Hamiltonian such that Hamilton's equations are equivalent to Newton's equation with the Lorentz force:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \& \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \qquad \Leftrightarrow \qquad m\mathbf{a} = z\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right)$$

- To this end, we introduced scalar and vector potentials ϕ and $\mathbf{A}$ such that

$$\mathbf{E} = -\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$$

- In terms of these potentials, the classical Hamiltonian function takes the form

$$H = \frac{\pi^2}{2m} + z\phi, \quad \boldsymbol{\pi} = \mathbf{p} - z\mathbf{A} \quad \leftarrow \text{kinetic momentum}$$

- Quantization is now accomplished in the usual manner, by the substitutions

$$\mathbf{p} \rightarrow -\mathrm{i}\hbar\boldsymbol{\nabla}, \quad H \rightarrow \mathrm{i}\hbar\frac{\partial}{\partial t}$$

- This gives the Schrödinger equation for a particle in an electromagnetic field:

$$\mathrm{i}\hbar\frac{\partial \Psi}{\partial t} = \frac{1}{2m}\left(-\mathrm{i}\hbar\boldsymbol{\nabla} - z\mathbf{A}\right)\cdot\left(-\mathrm{i}\hbar\boldsymbol{\nabla} - z\mathbf{A}\right)\Psi + z\phi\,\Psi$$

Electron spin

- The nonrelativistic Hamiltonian for an electron in an electromagnetic field is:

$$H = \frac{\pi^2}{2m} - e\phi, \quad \boldsymbol{\pi} = -\mathrm{i}\hbar\boldsymbol{\nabla} + e\mathbf{A}$$

- This description ignores a fundamental property of the electron: spin
- Spin was introduced by Pauli in 1927, to fit experimental observations:

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi = \frac{\pi^2}{2m} + \frac{e\hbar}{2m}\mathbf{B} \cdot \boldsymbol{\sigma} - e\phi$$

where $\boldsymbol{\sigma}$ contains three operators, represented by the two-by-two Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

- The Schrödinger equation now becomes a two-component equation:

$$\begin{pmatrix} \frac{\pi^2}{2m} - e\phi + \frac{e\hbar}{2m} B_z & \frac{e\hbar}{2m}\left(B_x - \mathrm{i}B_y\right) \\ \frac{e\hbar}{2m}\left(B_x + \mathrm{i}B_y\right) & \frac{\pi^2}{2m} - e\phi - \frac{e\hbar}{2m} B_z \end{pmatrix} \begin{pmatrix} \Psi_\alpha \\ \Psi_\beta \end{pmatrix} = E \begin{pmatrix} \Psi_\alpha \\ \Psi_\beta \end{pmatrix}$$

  - the two components are only coupled in the presence of an external magnetic field

- The introduction of spin by Pauli in 1927 may appear somewhat ad hoc
- By contrast, spin arises naturally from Dirac's relativistic treatment in 1928
  - is spin a relativistic effect?
- However, reduction of Dirac's equation to nonrelativistic form yields

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi = \frac{\pi^2}{2m} + \frac{e\hbar}{2m}\mathbf{B} \cdot \boldsymbol{\sigma} - e\phi \neq \frac{\pi^2}{2m} - e\phi$$

  - spin is therefore not a relativistic property of the electron
- Indeed, it is possible to take the factorized form

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi$$

  as the starting point for a nonrelativistic treatment, with unspecified operators $\boldsymbol{\sigma}$.
- All algebraic properties of $\boldsymbol{\sigma}$ then follow from the requirement $(\boldsymbol{\sigma} \cdot \mathbf{p})^2 = p^2$:

$$[\sigma_i, \sigma_j]_+ = 2\delta_{ij}, \quad [\sigma_i, \sigma_j] = 2\textstyle\sum_k \epsilon_{ijk}\sigma_k$$

  - these operators are represented by the two-by-two Pauli spin matrices
- To interpret $\boldsymbol{\sigma}$ we associate an intrinsic angular momentum (spin) with the electron:

$$\mathbf{s} = \hbar\boldsymbol{\sigma}/2$$

Molecular Hamiltonian

- The nonrelativistic Hamiltonian for an electron in an electromagnetic field

$$H = \frac{\pi^2}{2m} + \frac{e}{m}\mathbf{B}\cdot\mathbf{s} - e\phi, \quad \boldsymbol{\pi} = \mathbf{p} + e\mathbf{A}, \quad \mathbf{p} = -\mathrm{i}\hbar\boldsymbol{\nabla}$$

- Expanding π^2 and assuming the Coulomb gauge $\boldsymbol{\nabla}\cdot\mathbf{A} = 0$, we obtain

$$\begin{aligned}\pi^2\Psi &= (\mathbf{p} + e\mathbf{A})\cdot(\mathbf{p} + e\mathbf{A})\,\Psi = p^2\Psi + e\mathbf{p}\cdot\mathbf{A}\Psi + e\mathbf{A}\cdot\mathbf{p}\Psi + e^2A^2\Psi \\ &= p^2\Psi + e(\mathbf{p}\cdot\mathbf{A})\Psi + 2e\mathbf{A}\cdot\mathbf{p}\Psi + e^2A^2\Psi = \left(p^2 + 2e\mathbf{A}\cdot\mathbf{p} + e^2A^2\right)\Psi\end{aligned}$$

- In a molecule, the dominant electromagnetic contribution is from the nuclei:

$$\phi = \frac{1}{4\pi\epsilon_0}\sum_K \frac{Z_K e}{r_K} + \phi_{\text{ext}}$$

- Summing over all electrons and adding pairwise Coulomb interactions, we obtain

$$\begin{aligned}H = &\sum_i \frac{1}{2m}p_i^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{Ki}\frac{Z_K}{r_{iK}} + \frac{e^2}{4\pi\epsilon_0}\sum_{i>j} r_{ij}^{-1} && \leftarrow \text{zero-order Hamiltonian} \\ &+ \frac{e}{m}\sum_i \mathbf{A}_i\cdot\mathbf{p}_i + \frac{e}{m}\sum_i \mathbf{B}_i\cdot\mathbf{s}_i - e\sum_i \phi_i && \leftarrow \text{first-order Hamiltonian} \\ &+ \frac{e^2}{2m}\sum_i A_i^2 && \leftarrow \text{second-order Hamiltonian}\end{aligned}$$