Chem 542

Homework for Part 1: Dynamics and Electrodynamics

1. As discussed in the lecture notes, although the Lagrangian $\mathcal{L}$ is usually equal to K-V and H=K+V, this is not universally the case. An important exception is the Lagrangian for a charged particle in a field, necessary for deriving the basic spectroscopy formalism (two oppositely charged particles make a dipole!). The force is given by the equation

$$\mathbf{F} = q(\mathbf{E} + \frac{\mathbf{v}}{c} \times \mathbf{B}), \qquad [1]$$

Here, $\mathbf{E} = -\nabla\varphi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}$ and $\mathbf{B} = \nabla \times \mathbf{A}$ are the electric and magnetic fields, **v** is the particle velocity, and q the particle charge. $\varphi(r,t)$ is the scalar potential (basically the electrostatic potential energy); **A**(r,t) is the vector potential (less commonly encountered in chemistry; we'll discuss it in detail later in the course).

a. Using the relationships between (**E**,**B**) and (φ,**A**) given above and Lagrange's equation, show that the Lagrangian

$$\mathcal{L} = \frac{1}{2}mv^2 - q\varphi + \frac{q}{c}\mathbf{v}\cdot\mathbf{A} \qquad [2]$$

yields the correct Newtonian force law.
[Hint: use, $df(x,t)/dt = \partial f/\partial t + \partial f/\partial x \bullet dx/dt$ and $\mathbf{a}\times(\nabla\times\mathbf{b}) = \nabla(\mathbf{a}\cdot\mathbf{b}) - (\mathbf{a}\cdot\nabla)\mathbf{b}$]

b. Is $\mathcal{L}$ equal to K-V? Why?

c. Write down the conjugate momentum by taking the velocity derivative of eq. [2], and then derive the Hamiltonian H(**p**,**r**) =1/(2m) [**p** - q/c **A**]^2 + qφ. Is H equal to K+V?

2. As discussed in class, gauge transformations leave observables such as **E** and **B** invariant, although they may change quantities such as **A**, φ or Ψ. The Hamiltonian for the Schrödinger equation $H\Psi = i\hbar\,\partial\Psi/\partial t$ of a particle in an electromagnetic field is given using the electromagnetic+molecule Hamiltonian from the lecture notes by

$$\left\{\frac{1}{2m}(p - \frac{q}{c}A(x))^2 + q\varphi(x)\right\}\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)$$

where φ(x) (=$V(x)/q$) is the potential, $p = (\hbar/i)\partial/\partial x$ is the momentum operator, and A is the vector potential. For simplicity, let's do everything in one dimension, so $\nabla = \partial/\partial x$.

a. Show that if you substitute $\Psi_{new} = \Psi e^{i\chi(x,t)}$ into the above Schrödinger equation, Ψ_{new} obeys the identical Schrödinger equation

$$\left\{\frac{1}{2m}(p - \frac{q}{c}A_{new}(x))^2 + q\varphi_{new}(x)\right\}\Psi_{new}(x,t) = i\hbar\frac{\partial}{\partial t}\Psi_{new}(x,t),$$

but with $A_{new} = A + c_1\nabla\chi$ and $\varphi_{new} = \varphi + c_2\partial\chi / \partial t$. This is just the form of the gauge transformation derived in class. Determine the coefficients c_1 and c_2 for this transformation. [Hint: p and A do not commute, $\partial/\partial x(A\Psi e^{i\chi})$ has THREE terms from the chain rule, etc.]

b. Does the transformation of the wavefunction have an observable effect?