

Physics 251b
PROBLEM SET 5

Spring 2016

Due: Wednesday, April 27

Reading: Sakurai, Sec. 2.6 and 7.1-7.4

1. Gauge invariance and the Lorentz force

(a) The quantum mechanical expression for the current associated with a wave function $\psi(\vec{r}, t)$ reads

$$\vec{j}(\vec{r}, t) = \frac{\hbar}{2mi} \left[\psi^* \vec{\nabla} \psi - (\vec{\nabla} \psi) \psi^* \right] \quad (1)$$

Show that the substitution $\vec{\nabla} \rightarrow \vec{\nabla} - (iq/\hbar c) \vec{A}(\vec{r}, t)$ leads to a gauge-invariant current density and this new current operator satisfies the conservation law

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{j} = 0 \quad (2)$$

associated with the gauge invariant Schroedinger equation for a charged particle in an external electromagnetic field given by vector and scalar potentials $\vec{A}(\vec{r}, t)$ and $\phi(\vec{r}, t)$,

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \left(\vec{\nabla} - \frac{iq}{\hbar c} \vec{A}(\vec{r}, t) \right)^2 \psi(\vec{r}, t) + q\phi(\vec{r}, t) \psi(\vec{r}, t). \quad (3)$$

where ϕ and \vec{A} are related to \vec{E} and \vec{B} by

$$\vec{E} = -\vec{\nabla} \phi - \frac{1}{c} \frac{\partial \vec{A}}{\partial t}, \quad \vec{B} = \vec{\nabla} \times \vec{A} \quad (4)$$

(b) Is the solution of this Schroedinger equation in a static magnetic field invariant under time reversal? Explain your reasoning.

(c) Prove that the familiar Lorentz force acting on a particle with charge q and velocity

\vec{v} in electric and magnetic fields \vec{E} and \vec{B} , $\vec{F} = q(\vec{E} + \frac{\vec{v}}{c} \times \vec{B})$ follows from the classical

Euler-Lagrange equations associated with the Lagrangian

$$L(\vec{r}, \dot{\vec{r}} = \vec{v}) = \frac{1}{2} m \vec{v} \cdot \vec{v} - q\phi + \frac{q}{c} \vec{v} \cdot \vec{A} \quad (4)$$

Hint: the vector identity $\vec{C} \times (\vec{\nabla} \times \vec{D}) = \vec{\nabla}(\vec{C} \cdot \vec{D}) - (\vec{C} \cdot \vec{\nabla}) \vec{D}$ might be useful.

(Such a Lagrangian can be the starting point for a Feynman path integral treatment of a charged particle interacting with an electromagnetic field.)

2. Path integral for the harmonic oscillator

(a) Show, using path integral techniques that for a quantum harmonic oscillator with the Lagrangian

$$L = \frac{1}{2} m \dot{x}^2 - \frac{1}{2} m \omega^2 x^2 \quad (1)$$

that the propagator is given by

$$K(x, x', t, 0) = \tilde{A}(t) \exp \left\{ \frac{im\omega}{2\hbar \sin \omega t} [(x^2 - x'^2) \cos \omega t - 2xx'] \right\} \quad (2)$$

where $\tilde{A}(t)$ is an unknown function of t only. Recall that, given the eigenfunctions and the eigenvalues of the associated quantum Hamiltonian, we can also construct the propagator as follows:

$$K(x, x'; t, 0) = \sum_n \psi_n^*(x) \psi_n(x') e^{-iE_n t / \hbar}. \quad (3)$$

Consider now the reverse process (assuming the path integral approach has given us K directly) in the following:

(b) Set $x = x' = 0$. Assume that $\tilde{A}(t) = (m\omega / 2\pi i \hbar \sin \omega t)^{1/2}$ for the oscillator. By applying an appropriate Taylor series expansion to Eq (2) and comparing to Eq. (3), you should find that $E_n = \hbar\omega / 2, 5\hbar\omega / 2, 9\hbar\omega / 2$, etc. What happened to the energy levels in between?

(c) Now consider the extraction of eigenfunctions. Let $x = x'$ and by a similar technique, find E_0 , E_1 , $|\psi_0(x)|^2$, and $|\psi_1(x)|^2$.

3. Consider the H_2^+ ion, a molecule consisting of two protons and a single electron. In the adiabatic approximation (fixed distance $R = |\vec{R}_A - \vec{R}_B|$ between the two nuclei at positions \vec{R}_A and \vec{R}_B , each with charge $Z = +1$), the Hamiltonian for the single electron with coordinate \vec{r}_1 reads

$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{|\vec{r}_1 - \vec{R}_A|} - \frac{e^2}{|\vec{r}_1 - \vec{R}_B|} + \frac{e^2}{R}$$

The variational principle of quantum mechanics states that the ground state energy is given by minimizing

$$\int d^3r \varphi^*(\vec{r}) H \varphi(\vec{r}) - \varepsilon(R) \left[\int d^3r |\varphi(\vec{r})|^2 - 1 \right] \quad (1)$$

for an appropriately chosen electron trial wave function $\varphi(\vec{r})$. The ground state energy value $\varepsilon(R)$ can be regarded as a Lagrange multiplier that enforces the normalization condition

$$\int d^3r |\varphi(\vec{r})|^2 = 1 \quad (2)$$

(a) Assume a variational ground state wave function of the form

$$\varphi(\vec{r}_1) = \alpha\psi_A(1) + \beta\psi_B(1) \quad (3)$$

where α and β are real numbers and $\psi_A(1)$ and $\psi_B(1)$ are hydrogenic wave functions for an electron localized on proton A or B

$$\psi_A(1) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_{1A}/a_0}, \quad \psi_B(1) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r_{1B}/a_0} \quad (4)$$

where a_0 is the Bohr radius and $r_{1A} = |\vec{r}_1 - \vec{R}_A|$, $r_{1B} = |\vec{r}_1 - \vec{R}_B|$. From the variational principle, derive a set of coupled equations for α and β of the form

$$\begin{aligned} [V_{AA} + \zeta]\alpha + [V_{AB} + \zeta S]\beta &= 0 \\ [V_{BA} + \zeta S]\alpha + [V_{BB} + \zeta]\beta &= 0 \end{aligned} \quad (5)$$

where $\zeta = \varepsilon(R) - E_{1s} - e^2/R$. (E_{1s} is the ground state energy of an isolated hydrogen atom) and S is the overlap integral,

$$\begin{aligned} S(\rho) &= \frac{1}{\pi a_0^3} \int d^3r_1 e^{-(r_{1A} + r_{1B})/a_0} \\ &= \left(1 + \rho + \frac{1}{3}\rho^2\right) e^{-\rho} \\ &(\rho = R/a_0) \end{aligned} \quad (6)$$

Display, but do not evaluate, similar integral expressions for V_{AA} , V_{AB} , V_{BA} and V_{BB} .

(b) Assume that the ground state electron wave function is symmetric, i.e. that $\alpha = \beta$ in Eq. (3), and derive an expression for φ and hence the ground state energy of the form

$$\varepsilon(R) = E_{1s} + \frac{e^2}{R} f(R/a_0) \text{ and determine the function } f(\rho), \text{ where } \rho = R/a_0.$$

Hint: The results

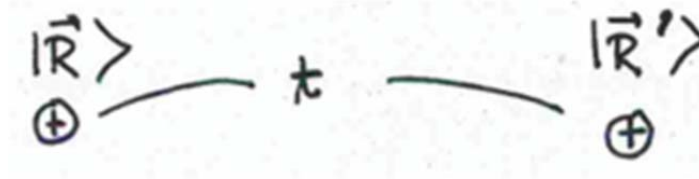
$$\int \frac{\psi_A^2(1)}{r_{B1}} d^3r_1 = \frac{1}{R} [1 - (1 + \rho)e^{-2\rho}], \quad \int \frac{\psi_A(1)\psi_B(1)}{r_{A1}} d^3r_1 = \frac{1}{a_0} (1 + \rho)e^{-\rho} \quad (7)$$

might be useful.

(c) Using the result of part (b), show that there is a critical value ρ^* such that for $\rho < \rho^*$ the nuclei in H_2^+ repel while for $\rho > \rho^*$ they attract. What is ρ^* ?

4. Tight binding model of the hydrogen molecule

(a) A simple model for the hydrogen molecule H_2 is sketched below



Electrons can sit either on the proton at $|\vec{R}\rangle$ or on the proton at $|\vec{R}'\rangle$. The Hamiltonian of a single electron is

$$h = \begin{pmatrix} \epsilon & -t \\ -t & \epsilon \end{pmatrix} \begin{pmatrix} |\vec{R}\rangle \\ |\vec{R}'\rangle \end{pmatrix} \quad (1)$$

where t is a real, positive, one electron hopping matrix element. How would you expect t to behave as $|\vec{R} - \vec{R}'| \rightarrow \infty$? Show that the one-electron stationary levels are

$$\frac{1}{\sqrt{2}}(|\vec{R}\rangle \mp |\vec{R}'\rangle) \quad (2)$$

with corresponding energy values $\epsilon \pm t$.

Thus far, we have neglected entirely the interaction of an electron site $|\vec{R}\rangle$ with the proton on site $|\vec{R}'\rangle$ in this treatment. However, a simple way to treat the electron-electron interactions is to assume that there is an additional energy which is $U > 0$, when two electrons (with opposite spin to satisfy the Pauli exclusion principle) are on the same proton, and zero otherwise. As a first approach to the *two*-electron problem (i.e., the H_2 molecule) form the singlet (spatially symmetric) ground state, putting both electrons into the one-electron level of lowest energy, to get a total energy of $2(\epsilon - t)$. This “Hartree approximation” ignores entirely the interaction energy U , arising when two electrons are found on the same proton. The simplest way to improve upon the estimate $2(\epsilon - t)$ is to add the energy U , multiplied by the probability of actually finding two electrons on the same proton, when the molecule is in the Hartree approximation to the ground state. Find this probability, and determine the resulting ground-state energy E_H .

(b) The full set of singlet (spatially symmetric) states of the two-electron problem are:

$$\Phi_0 = \frac{1}{\sqrt{2}}(|\vec{R}\rangle|\vec{R}'\rangle + |\vec{R}'\rangle|\vec{R}\rangle) \quad (3)$$

$$\Phi_1 = |\vec{R} > |\vec{R} >, \Phi_2 = |\vec{R}' > |\vec{R}' > \quad (4)$$

where $|\vec{R} > |\vec{R}' >$ places electron 1 on the ion at \vec{R} , and electron 2 on the ion at \vec{R}' , etc. Show that the approximate ground state wave function in the Hartree approximation can be written in terms of the states (3) & (4) as

$$\Phi_H = \frac{1}{\sqrt{2}}\Phi_0 + \frac{1}{2}(\Phi_1 + \Phi_2) \quad (5)$$

Explain why the matrix elements of the full interacting two-electron Hamiltonian,

$$H = h_1 + h_2 + V_{12} \quad (6)$$

in the space of these singlet states are $H_{ij} = \langle \Phi_i | H | \Phi_j \rangle$, where the matrix elements $\{H_{ij}\}$ have the form

$$\begin{pmatrix} H_{00} & H_{01} & H_{02} \\ H_{10} & H_{11} & H_{12} \\ H_{20} & H_{21} & H_{22} \end{pmatrix} = \begin{pmatrix} 2\varepsilon & -\alpha t & -\alpha t \\ -\alpha t & 2\varepsilon + U & 0 \\ -\alpha t & 0 & 2\varepsilon + U \end{pmatrix} \quad (7)$$

In Eq. (6), h_1 and h_2 refer to a Hamiltonian like (1) for each electron, and V_{12} represents the electron-electron interaction. Assume that two electrons cannot simultaneously hop from $|\vec{R} >$ to $|\vec{R}' >$. Note that the diagonal elements in the states Φ_1 and Φ_2 that place two electrons on the same proton contain the extra Coulomb repulsion U ; the Coulomb repulsion is not present in the diagonal element in the state Φ_0 , since in Φ_0 the electrons are on different protons. Assume that this appearance of U is the only effect of the electron-electron interaction V_{12} . Determine the constant α appearing in Eq. (7).

(c) Find the exact ground-state energy E_{exact} of the Hamiltonian (7). How does this energy behave as $|\vec{R} - \vec{R}'| \rightarrow \infty$? Plot this energy, and the Hartree ground state energy E_H as functions of U (for fixed ε and t). Comment on the behavior for large and small U/t and why it is physically reasonable.

(d) Show that the exact ground state of the Hamiltonian (32.38) is (to within a normalization constant) takes the form

$$\Phi_0 = \frac{1}{\sqrt{2}}\Phi_0 + f(u)\frac{1}{2}(\Phi_1 + \Phi_2) \quad (8)$$

and determine the function of $f(u)$. What is the probability in this state of finding two electrons on the same proton? Plot your answer as a function of U (for fixed ε and t) and comment on its behavior for small and large U/t .