Handed Out: Thursday 2015/04/09
Due: Thursday 2015/04/16 (before class)

1. (30 pts) **Gauge Invariance in Quantum Mechanics**. Consider a single particle of mass m and charge $Z\, q_e$. In the presence of a vector potential $\boldsymbol{A}(\boldsymbol{r},t)$ and scalar potential $\phi(\boldsymbol{r},t)$, the quantum hamiltonian operator is

$$\hat{\mathcal{H}} = \frac{1}{m}(\hat{\boldsymbol{p}} - Zq_e\boldsymbol{A})\cdot(\hat{\boldsymbol{p}} - Zq_e\boldsymbol{A}) + Zq_e\phi + V(\boldsymbol{r}) \quad (1)$$

which equals

$$\hat{\mathcal{H}} = \frac{1}{m}(-i\hbar\nabla - Zq_e\boldsymbol{A})\cdot(-i\hbar\nabla - Zq_e\boldsymbol{A}) + Zq_e\phi + V(\boldsymbol{r}). \quad (2)$$

The time-dependent Schrödinger equation for the state vector $|\psi\rangle$ is

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{\mathcal{H}}\,|\psi\rangle \quad (3)$$

Under a gauge transformation

$$\boldsymbol{A} \to \boldsymbol{A}' = \boldsymbol{A} - \nabla\chi \qquad \phi \to \phi' = \phi + \frac{\partial\chi}{\partial t} \quad (4)$$

with arbitrary $\chi(\boldsymbol{r},t)$, the hamiltonian transforms to

$$\hat{\mathcal{H}} \to \hat{\mathcal{H}}' = \frac{1}{m}(-i\hbar\nabla - Zq_e\boldsymbol{A}')\cdot(-i\hbar\nabla - Zq_e\boldsymbol{A}') + Zq_e\phi' + V(\boldsymbol{r}) \quad (5)$$

Define the transformed state

$$|\psi'\rangle \equiv e^{-i\alpha}\,|\phi\rangle \quad (6)$$

where $\alpha = \alpha(\boldsymbol{r},t)$. Determine $\alpha(\boldsymbol{r},t)$ such that the transformed Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi'\rangle = \hat{\mathcal{H}}'\,|\psi'\rangle \quad (7)$$

is equivalent to the original equation. Hint: consider the transformed momentum operator

$$\hat{\boldsymbol{p}}' = e^{+i\alpha}\,\hat{\boldsymbol{p}}\,e^{-i\alpha}. \quad (8)$$

Show that, for this choice of α, matrix elements are invariant; that is

$$\langle\psi|(\hat{\boldsymbol{p}} - Zq_e\boldsymbol{A})|\psi\rangle = \langle\psi'|(\hat{\boldsymbol{p}} - Zq_e\boldsymbol{A}')|\psi'\rangle \quad (9)$$

This result shows that the expectation values of observables are unaffected by gauge transformations.

— *see Cohen-Tannoudji et al. Compliment C_{III}*

2. (35 pts) Let us calculate the **photoionization cross section of the hydrogen atom** from first principles.

The atom is irradiated with photons of energy $E_0 = \hbar\omega = 20$ eV. The atom absorbs a photon and ejects an electron. Before ionization, the electron is in the ground-state orbital of the hydrogen atom. After ionization, the electron is a free particle with a wavefunction of $\psi = \exp(i\boldsymbol{k'}\cdot\boldsymbol{r})/\sqrt{V}$ where $\boldsymbol{k}'$ is the final electron wavevector. Here k' is related to photoelectron's translational energy by $E' = \hbar^2 k'^2/2m$; energy conservation demands that $E_0 = \mathrm{IP} + E'$ where IP is hydrogen's ionization potential.

Derive an expression for the differential absorbtion rate $dw/d\Omega$ for absorbtion of light by a ground state hydrogen atom. In determining the rate expression, the relevant state density should be taken to be the product of the photon and electron state densities. Units analysis helps relate the Fermi's-Golden-Rule transition rate w to the cross section σ and the flux of incoming photons:

$$dw\,[\frac{1}{\mathrm{s}}] = d\sigma\,[\mathrm{m}^2] \times \_\_\,[\frac{\mathrm{J}}{\mathrm{m}^3}] \times \_\_\,[\frac{\mathrm{photon}}{\mathrm{J}}] \times \_\_\,[\frac{\mathrm{m}}{\mathrm{s}}]$$

There is then a nasty integral to work out. The following formula should help:

$$\int_0^\infty r^2\,dr \int_0^{2\pi} d\phi \int_0^\pi \sin\theta\,d\theta\,e^{-i\,\boldsymbol{k}'\cdot\boldsymbol{r}}\,r\,\cos\theta\,e^{-r/a_0} = -i\,\frac{32\pi k'}{a_0(a_0^{-2} + k'^2)^3} \quad (10)$$

Once you have $dw/d\Omega$, you can determine the absolute photoionization cross section σ [m^2] by an integration over scattering angles.

Determine the photoionization cross section σ of the hydrogen-atom ground state at $\hbar\omega = 20$ eV. Plot σ versus E'.

— *adapted from Schatz and Ratner Chapter 5, Problem 3.*

3. (35 pts) Let's use **Fermi's-Golden Rule** to calculate the cross section for rotational excitation of a molecule caused by a collision with another molecule.

Consider a collision of an ion such as H^+ with H_2. At large separations R between the ion and the molecule (where the straight-line trajectory model is accurate), the ion-molecule interaction potential has the general form:

$$V(R,\theta) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{R^4}[V_0 + V_2 P_2(\cos\theta)] \quad (11)$$

where

$$V_0 = \frac{\alpha_\parallel + 2\alpha_\perp}{3} \tag{12}$$

$$V_2 = \frac{\alpha_\parallel - \alpha_\perp}{3} \tag{13}$$

$$P_2(\cos\theta) = \frac{3\cos^2\theta - 1}{2} \tag{14}$$

In this formula, e is the electronic charge, $\alpha_\parallel$ and $\alpha_\perp$ are the parallel and perpendicular static polarizabilities of the H_2 molecule, and ϵ_0 is the vacuum permittivity. Since $V(R, \theta)$ depends on orientation angle θ between R and the diatomic axis r, the ion-molecule coupling will cause a rotational excitation and deexcitation of H_2.

(a) Assuming a straight-line trajectory, derive an expression for the transition probability

$$H_2(v = 0, j = 0, m_j = 0) \longrightarrow H_2(v = 0, j = 2, m_j = 0, \pm 1, \pm 2). \tag{15}$$

Evaluate this probability explicitly for $b = 2$, 10, 50Å and $E_0 = 10$ eV using $\alpha_\parallel = 1.0$ Å^3 and $\alpha_\perp = 0.63$ Å^3. Since the rotational spacing is small, you can assume when evaluating the transition probability that $\omega_{km} = 0$.

(b) To integrate the result of part (a) over impact parameters to get a cross section, it is necessary to truncate the integration at a minimum impact parameter b_0. The minimum impact parameter b_0 corresponds to the "radius" of H_2 and represents the distance of closest approach between H_2 and H^+. Assuming that $b_0 = 2$ Å, what are the cross sections for the above-mentioned transitions at 10 eV?

— *reference: Schatz and Ratner Chapter 4 (especially 4.3.2)*