PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 6 EXERCISE CLASSES (2-6 March 2020)

What are Sample Questions (SQs)? TA will discuss the **SAMPLE QUESTIONS** in exercise classes. The Sample Questions are designed to serve several purposes. They either review what you have learnt in previous courses, supplement our discussions in lectures, or closely related to the questions in an upcoming Problem Set. You should attend one exercise class session per week. You are encouraged to think about (or work out) the sample questions before attending exercise class and ask the TA questions.

Students: The SQs are related to the time-independent perturbation theory. Read the summary first.

Non-degenerate Perturbation Theory - Summary of Key Results

Given $\hat{H} = \hat{H}_0 + \hat{H}'$, but the TISE problem $\hat{H}\psi = E\psi$ cannot be solved analytically. The unperturbed problem $\hat{H}_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$ is, fortunately, solvable and the whole sets of $\{\psi_n^{(0)}\}$ and $\{E_n^{(0)}\}$ are known. Here, $\hat{H}'$ is the **perturbation term** and the unperturbed problem is meant to be a big portion of the problem. The most important result of **non-degenerate perturbation theory** is an approximate formula for the n-th eigenvalue of the problem

$$H\psi_n = E_n\psi_n \tag{1}$$

up to the second order given by

$$\begin{aligned} E_n &\approx E_n^{(0)} + \langle\psi_n^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle + \sum_{i\neq n} \frac{|\langle\psi_i^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle|^2}{E_n^{(0)} - E_i^{(0)}} \\ &= \underbrace{E_n^{(0)}}_{0th\ order} + \underbrace{\int \psi_n^{*(0)}\hat{H}'\psi_n^{(0)}d\tau}_{first\ order} + \underbrace{\sum_{i\neq n} \frac{|\int \psi_i^{*(0)}\hat{H}'\psi_n^{(0)}d\tau|^2}{E_n^{(0)} - E_i^{(0)}}}_{second\ order} \end{aligned} \tag{2}$$

The first-order theory to the n-th eigenstate is

$$\psi_n \approx \psi_n^{(0)} + \sum_{i\neq n} \frac{\int \psi_i^{*(0)}\hat{H}'\psi_n^{(0)}d\tau}{E_n^{(0)} - E_i^{(0)}}\,\psi_i^{(0)} \tag{3}$$

We derived these formulas in class. It is more important that you **understand the meaning of the symbols** in Eqs.(2) and (3) and **how to apply the formulas** than to derive them.

Applying the results requires two levels of maturity in physics and mathematics. (a) We need to set up the problem (i.e., identify $\hat{H}_0$ and $\hat{H}'$) and then write down the integrals explicitly in Eq. (2) and Eq. (3). (b) We need to do the integrals. For (a), after identifying $\hat{H}_0$, we need the exact solutions to TISE of $\hat{H}_0$. We know only a few of them, including the infinite well, harmonic oscillator (1D,2D,3D), rigid rotors, and hydrogen atom. For (b), we need to do many integrals involving sine and cosine functions (infinite well), Hermite polynomials (harmonic oscillator), $e^{im\phi}$ and $Y_{lm}(\theta,\phi)$ (rotors), and $\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$ (hydrogen atom). Some integrals are hard to do, but there are integral tables and web sites to come to help. The point is that you shouldn't let the mathematics ruin your appreciation to the cleverness of making approximations. The SQs here apply the perturbation results.

SQ13: 1st and 2nd order perturbation theory applied to an exactly solvable problem (harmonic oscillator)

SQ14: Shifts in hydrogen atom energies due to relativistic correction to kinetic energy - 1st order perturbation theory

SQ13 *Harmonic Oscillator – an exactly solvable problem treated by 1st and 2nd order perturbation theory*

Consider an 1D harmonic oscillator in which the potential energy function is $U(x) = \frac{1}{2}k(1+\epsilon)x^2$, where ϵ is meant to be $\epsilon \ll 1$. This is just a harmonic oscillator with spring constant $k(1+\epsilon)$ instead of k and therefore it is exactly solvable. **Write down the exact eigenvalues** of the problem (no derivation needed).

Knowing the exact results, we actually don't need the perturbation theory. It is, however, interesting to see how well perturbation theory works.

(a) The exact eigenvalues **can be expanded** into a power series in ϵ because $\epsilon \ll 1$. **Do it.**

(b) Taking the unperturbed problem as defined by the Hamiltonian $\hat{H}_0$ with

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 \tag{4}$$

so that the perturbed problem as

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}k(1+\epsilon)x^2 = \hat{H}_0 + \hat{H}' \ , \tag{5}$$

identify the perturbation term $\hat{H}'$ and **obtain** the 1st order perturbation in the energy for **all states**.

(c) Next consider only the **ground state**. **Find the 2nd order perturbation to the ground state energy**. Hence, **write down** the ground state energy including 0th, 1st, and 2nd order terms.

(d) **Compare** the perturbation result with the exact result in part (a) to the same order.

(e) **(Optional for TA, just for fun) How about** the 1st order correction to the ground state wavefunction?

[Remark: This is Problem 6.2 and Problem 6.4(b) in Griffiths' *Introduction to Quantum Mechanics.*]

SQ14 *Non-degenerate perturbation theory: 1st order correction to hydrogen atom energies due to relativistic correction to the kinetic energy*

Background – Schrödinger solved the hydrogen atom problem in 1926 and found the famous $-13.6/n^2$ (in eV) energies as observed in hydrogen spectrum (Lyman, Balmer,... series). In SQ2, we used the reduced mass to make the numbers close to spectroscopic data. In SQ4, we showed that there is a relativistic correction term in the Hamiltonian when we include one more term in the kinetic energy, i.e. $T \approx p^2/2m + (\textit{correction})$. This SQ treats the (*correction*) term as perturbation.

The result is important in that (i) the correction is tiny, and (ii) the small correction is characterized by the **fine structure constant squared**, or α^2. We met the fine structure constant $\alpha \approx 1/137$ in SQ4.

(a) In SQ4, we found that

$$T \approx \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} \ , \tag{6}$$

keeping a leading correction term due to relativity. Hence, using the corrected kinetic energy term in the Schrödinger Equation of a hydrogen atom, we have

$$H = \underbrace{\frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}}_{\text{solved exactly}} \qquad \overbrace{-\frac{p^4}{8m^3c^2}}^{\text{correction to handle}} \qquad = \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}\right) - \frac{p^4}{8m^3c^2} = H_0 + H' \tag{7}$$

The unperturbed $\hat{H}_0$ problem is analytically solvable. The energy eigenvalues are the famous $E_n^{(0)} \sim -13.6/n^2$ in eV and the eigenstates are $\psi^{(0)}_{n\ell m_\ell}(r,\theta,\phi)$.

Apply 1st order perturbation theory (don't do the integrals at this point) to **write down the correction to the hydrogen atom energies**.

(b) **Evaluate (or simply give the results of)** the integrals and hence **give an explicit expression of the first order shift in energy** due to $\hat{H}'$. It is important to **point out how small** the correction term is, in comparison to the unperturbed energy.

Hints to TA: The $\hat{H}'$ term can be handled as follows. (i) **Show** that the 1st order perturbation in energy is related to the expectation value of $\langle(\hat{H}_0 - U(r))^2\rangle$ with respect to the unperturbed hydrogen atom states, where $U(r) = -e^2/(4\pi\epsilon_0 r) = -e^2/(\kappa_0 r)$. (ii) Hence, **show** that it amounts to evaluating the value of expectation values $\langle 1/r\rangle$ and $\langle 1/r^2\rangle$ for different $\psi^{(0)}_{n\ell m_\ell}(r,\theta,\phi)$. (iii) These are standard integrals of hydrogen atom physics, although not easy to do. I looked them up from books and found that

$$\langle\frac{1}{r}\rangle_{n\ell m_\ell} = \frac{1}{n^2 a_0} \quad , \quad \langle\frac{1}{r^2}\rangle_{n\ell m_\ell} = \frac{1}{(\ell+\frac{1}{2})n^3 a_0^2} \tag{8}$$

where the subscript (n,ℓ,m_ℓ) labels the state in which the expectation value is evaluated and $a_0 = \kappa_0\hbar^2/(me^2)$ is the Bohr radius.

Use these results to obtain the first order correction $E^{(1)}_{n\ell m_\ell}$. Most importantly, **show** that the magnitude of the correction is governed the **fine structure constant squared** α^2, which is about $(1/137)^2$ of the unperturbed energy $E_n^{(0)}$. This is therefore tiny. **Though small, spectroscopy (atomic spectrum) is sensitive enough that we need to consider such corrections.**

[For TA: It is more important to point out how those integrals emerge from the perturbation formula and what those integrals are. You need not carrying out the expectation value calculations in Eq. (9), unless you want to show off your technique in an appendix.]

[Further remark: Those of you with sharp eyes may start worrying why we could apply 1st order (non-degenerate) result here, as hydrogen energy levels carry degeneracy in general, e.g. there are several $(n = 2)$ states with the same energy $-13.6/4$ eV. This is a tricky question that can be explained by even sharper eyes on the form of the perturbation $\hat{H}'$. For the moment, don't worry about it as the reason is a bit technical for some students. Another remark is that there will be another relativistic correction term related to the spin of the electron that we have not considered.]