PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 4 EXERCISE CLASSES (1-5 February 2021)

You are encouraged to think about (or work out) the sample questions before attending exercise class and ask the TA questions. Your should attend one exercise class session per week.

SQ6: Relativistic correction to the kinetic energy term - First order perturbation theory for the H-atom energies
SQ7: Matrix elements of x^α between harmonic oscillator states

SQ6 *Relativistic correction to the kinetic energy term - First order perturbation theory for H-atom energies* **(Following up SQ2)**

Background – In SQ2, we showed that starting from

$$T = \sqrt{p^2c^2 + m^2c^4} - mc^2 \tag{1}$$

for the kinetic energy and expanding the expression in powers of the small parameter (p/mc), the leading correction term to the kinetic energy T is

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

Within the context of the hydrogen atom problem, we have a modified Hamiltonian

$$\hat{H} = \frac{p^2}{2m} + V(r) - \frac{p^4}{8m^3c^2} = \left(\frac{p^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}\right) - \frac{p^4}{8m^3c^2} = \hat{H}_0 + \hat{H}'. \tag{3}$$

Without the relativistic term, the Schrödinger Equation gives solutions of the form $\psi_{n\ell m_\ell}$ with eigenvalues (allowed energies) given by $E_n^{(0)} \sim -13.6/n^2$ in eV. This is, therefore, a perfect situation to study the effect of the relativistic correction term $\hat{H}'$ using the first-order perturbation theory. The calculation is interesting for the following reasons: (a) We will investigate the **spin-orbit interaction** in atoms. It is another relativistic effect. Therefore, it will be fair to also see how this relativistic correction term alters the known zeroth order H-atom energies. (b) It is easy to write down what to evaluate as $E_{rel}^{(1)}$. (c) It is, however, NOT easy to evaluate $E_{rel}^{(1)}$. Nonetheless, $E_{rel}^{(1)}$ can be evaluated **analytically** for **all** H-atom states. (d) It is **a result students need to know**. (e) But **students are not expected to be able to do the integrals involved in this SQ for exam purposes**.

TAs: Apply the first order perturbation theory and **show** that the first order correction in energy due to the relativistic term is

$$E_{rel}^{(1)} = -E_n^{(0)} \left(\frac{E_n^{(0)}}{2mc^2}\right) \left\{\frac{4n}{\ell + \frac{1}{2}} - 3\right\} \tag{4}$$

TAs: Please follow the logic flow. (a) **Point out** that the we need to do an integral $\langle\psi_{n\ell m_\ell}|p^4|\psi_{n\ell m_\ell}\rangle$ in applying 1st order perturbation theory. (b) **Show** that the integral can be related to the expectation values of $V(r)$ and $V(r)^2$, i.e., $\langle\psi_{n\ell m_\ell}|V|\psi_{n\ell m_\ell}\rangle$ and $\langle\psi_{n\ell m_\ell}|V^2|\psi_{n\ell m_\ell}\rangle$, where $V(r)$ is the Coulomb potential energy function. (c) Then invoke the following integrals

$$\left\langle \frac{1}{r} \right\rangle = \int \psi^*_{n\ell m_\ell} \frac{1}{r} \psi_{n\ell m_\ell} d^3r = \frac{1}{n^2 a} \tag{5}$$

and

$$\left\langle \frac{1}{r^2} \right\rangle = \int \psi^*_{n\ell m_\ell} \frac{1}{r^2} \psi_{n\ell m_\ell} d^3r = \frac{1}{(\ell + \frac{1}{2})\, n^3 a^2} \tag{6}$$

to obtain the answer. Here, a is the Bohr radius.

TAs: Illustrate how small the energy correction is, relative to $E_n^{(0)}$ (for example for the ground state) and stress that $E_{rel}^{(1)}$ depends on n and ℓ in general. You may want to show students the proof of Eqs.(5) and (6) in an appendix.

SQ7 *Harmonic oscillator physics and matrix elements using operators*

This serves as a review on what you did in harmonic oscillators in QM I and to prepare for evaluating matrix elements of x, x^2, x^3 and x^4 between harmonic oscillator wavefunctions in applying approximation methods. Generally, we need integrals of the forms

$$\int \psi^*_m(x)\, \hat{x}^\alpha\, \psi_n(x)\, dx \quad \text{and} \quad \int \psi^*_m(x)\, \hat{p}^\alpha\, \psi_n(x)\, dx \tag{7}$$

where $\psi_n(x)$ is the n-th eigenstate of the harmonic oscillator with energy $(n + \frac{1}{2})\hbar\omega$ (here $n = 0, 1, 2, \ldots$), and $\hat{x}$ and $\hat{p}$ are the position and momentum operators, respectively. Here, TA will work out the $\alpha = 1$ and $\alpha = 2$ cases.

The Hamiltonian of a harmonic oscillator is:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2 \tag{8}$$

In this form, it is tempting to "factorize" the Hamiltonian. It is of the form of $(c^2 + d^2) = (c + id)(c - id)$. Thus, rather "naturally", one can define two new operators which are linear combinations of $\hat{x}$ and $\hat{p}$ invoking $i = \sqrt{-1}$ as:

$$\begin{aligned} \hat{a} &= \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} + \frac{i}{m\omega} \hat{p} \right) \\ \hat{a}^\dagger &= \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{x} - \frac{i}{m\omega} \hat{p} \right) \end{aligned} \tag{9}$$

TA: **Find** the commutator $[\hat{a}, \hat{a}^\dagger]$. **Show** that the following Hamiltonian

$$\hat{H} = \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) \hbar\omega \tag{10}$$

is just the harmonic oscillator Hamiltonian in Eq. (8). The form of Eq. (10) is convenient in that there is a set of eigenstates denoted by $|n\rangle$ that satisfies $\hat{a}^\dagger \hat{a} |n\rangle = n|n\rangle$, with $n = 0, 1, 2, \ldots$ (non-negative integrals). Immediately, we see that

$$\hat{H}|n\rangle = \left(n + \frac{1}{2} \right) \hbar\omega\, |n\rangle \tag{11}$$

and thus the state $|n\rangle$ is the n-th eigenstate of the harmonic oscillator. They are orthonormal. Writing the state $|n\rangle$ out in x-coordinate gives the oscillator wavefunctions $\psi_n(x)$, which are the Hermite polynomials multiplying into a Gaussian function. More important to the purpose here are the following properties:

$$\begin{aligned} \hat{a}^\dagger\, |n\rangle &= \sqrt{n+1}\, |n+1\rangle \\ \hat{a}\, |n\rangle &= \sqrt{n}\, |n-1\rangle \end{aligned} \tag{12}$$

Because of these special effects, $\hat{a}^\dagger$ is called the raising (creation) operator and $\hat{a}$ is called the lowering (annihilation) operator.

TAs: Our goal is to work out the integrals in Eq. (7). To proceed, use Eq. (9) to **express** $\hat{x}$ and $\hat{p}$ in terms of $\hat{a}$ and $\hat{a}^\dagger$. Hence, **work out**

$$\langle m|\hat{x}|n\rangle \quad \text{and} \quad \langle m|\hat{p}|n\rangle \tag{13}$$

which are Eq. (7) for $\alpha = 1$.

Here is the physics. The integrals $\langle m|\hat{x}|n\rangle$ and $\langle m|\hat{p}|n\rangle$ are related to possible transitions from state $|n\rangle$ to state $|m\rangle$ due to a perturbation such as an incident light. But $\langle m|\hat{x}|n\rangle$ is related to $\langle m|\hat{a}|n\rangle$ which requires $m = n-1$ to be non-vanishing **and** $\langle m|\hat{a}^\dagger|n\rangle$ which requires $m = n+1$ to be non-vanishing. Therefore, $\hat{x}$ **can only connect** oscillator state n to its neighbors $n-1$ and $n+1$. This is the take-home message. An application of the result is that a transition between vibrational (oscillator) states due to light can only occur between state $|n\rangle$ and the neighboring states $|n-1\rangle$ and $|n+1\rangle$, the so-called $\Delta n = \pm 1$ **selection rule**. We will use the rule in understanding **molecular spectrum**. [Of course, one can plug in wavefunctions and do the integrals. It is one's taste in judging which method is more elegant.]

TAs: **Also work out** $\langle m|\hat{x}^2|n\rangle$.

[Hint: An easy way is to make use of the completeness of the whole set of eigenstates, i.e., $\sum_j |j\rangle\langle j| = 1$ and insert it between $\hat{x}\hat{x}$.]

Remarks (TA: Don't work these out): How about $\langle m|\hat{x}^3|n\rangle$ or $\langle m|\hat{x}^4|n\rangle$? Easy! Keep on inserting 1's!