PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 10 EXERCISE CLASSES (6 - 10 April 2020)

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 closed 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.

Progress: In Week 9, we discussed the anti-symmetric requirement on multi-electron wavefunctions, the Slater determinant form invoking single-electron states, Pauli Exclusion Principle, Helium (1s,2s) excited states, exchange integral and the origin of magnetism. After the Reading Week, we will discuss the periodic table, transitions between atomic states through absorption and emission of light in Week 10. We will see how quantum mechanics gives the selection rules, the condition that the incident light must of the right frequency to stimulate absorption and emission, and what governs the intensities of spectral lines.

SQ23 - Three-electron wavefunctions - Slater determinants
SQ24 - Electric dipole matrix elements, forbidden and allowed transitions in hydrogen atom between $n = 1$ and $n = 2$ states

SQ23 *Three-electron wavefunctions - Slater determinants*

Consider three electrons (three fermions) in three **different** single-particle states (after using IPA say) labelled a, b, c with wavefunctions ϕ_a, ϕ_b and ϕ_c. [Note: Sometimes, the label a could already carry a spin information, e.g. "1s-up" or "1s↑". For example, the ground state of lithium atom can be thought to have electrons in 1s-up, 1s-down, and 2s-up (could be 2s-down).]

A wavefunction that has the correct anti-symmetric property is given by a **Slater determinant**

$$\psi(1,2,3) \propto \begin{vmatrix} \phi_a(1) & \phi_b(1) & \phi_c(1) \\ \phi_a(2) & \phi_b(2) & \phi_c(2) \\ \phi_a(3) & \phi_b(3) & \phi_c(3) \end{vmatrix} \tag{1}$$

Here, 1, 2, and 3 are the coordinates of particles 1, 2, 3, respectively. This SQ reminds you of some basic determinant properties and illustrates that determinants are useful.

(a) **Find the normalization factor** in front of the expression, given that the single-particle states ϕ's are properly normalized. [Remark: This is a counting problem. The normalization factor is related to the number of terms in the right-hand side of Eq. (1).]

(b) **Show** that $\psi(1,2,3)$ is anti-symmetric with respect to interchanging the coordinates of any two particles.

(c) There is a problem if we assign two particles into the **same single-particle state**. **Illustrate** what the problem is when two of the three **states** are identical. Hence, **point out** that the Pauli Exclusion Principle stating "two electrons cannot occupy the same (single-electron) state" follows follows from Eq. (1).

(d) Another important and interesting observation from Eq. (1) is that two fermions tend to **avoid each other**. For illustrative purpose, let's simply take the coordinates to be

spatial coordinates $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$ for three fermions and hence ψ is a spatial wavefunction of three fermions. In this case, Eq. (1) becomes

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \propto \begin{vmatrix} \phi_a(\mathbf{r}_1) & \phi_b(\mathbf{r}_1) & \phi_c(\mathbf{r}_1) \\ \phi_a(\mathbf{r}_2) & \phi_b(\mathbf{r}_2) & \phi_c(\mathbf{r}_2) \\ \phi_a(\mathbf{r}_3) & \phi_b(\mathbf{r}_3) & \phi_c(\mathbf{r}_3) \end{vmatrix} \tag{2}$$

Show that when any two fermions take on the same location in real space, the spatial wavefunction vanishes. By invoking the Born's interpretation of the wavefunction, **state what it means**. [Remarks: Contrasting what we do here with part (c), the wavefunction vanishes only for some particular coordinates of the particles. This is NOT a problem, because the wavefunction does not vanish for other choices of the coordinates. Thus, an **antisymmetric spatial wavefunction has the property that the particles tend to avoid each other**. This is an important concept. Note that this property comes entirely from the anti-symmetric form of the wavefunction. This avoidance of particles is there **even there is no physical interaction** between particles. This is why ideal (non-interacting) Fermi gas and ideal (non-interacting) Bose gas behave so differently.]

[Remarks: John C. Slater made important contributions to the understanding of matter (atoms, molecules, solids) using quantum mechanics. He wrote several classics textbooks. See *Quantum Theory of Atomic Structure* (2 volumes), *Quantum Theory of Matter*, *Quantum Theory of Molecules and Solids* (2 volumes) **all** by Slater. There are other books on Mechanics and Electromagnetism. Slater was the Physics Department Chairman of MIT from 1930-1950 and built it up to what we know it now.]

SQ24 *Hydrogen atom's "Electric Dipole Matrix element" for transitions between* $n = 1$ *and* $n = 2$ *states*

We will soon see that a perturbation term $\hat{H}'(\mathbf{r}, t)$, which is in principle depending on time and spatial coordinates $\mathbf{r}$, is responsible for inducing (stimulating) a transition between atomic states. When a system is initially in an eigenstate $\psi_{initial}$, only $\hat{H}'$ can take the system away from $\psi_{initial}$. Thus $(\hat{H}'\psi_{initial})$ has a part that is not the initial state. The probability amplitude of finding the system in another eigenstate ψ_{final} after a time t that $\hat{H}'$ has been applied to the system is given by the projection of $\hat{H}'\psi_{initial}$ onto ψ_{final}, i.e.,

$$a_f(t) \propto \int \psi^*_{final}(\mathbf{r})\; \hat{H}'\; \psi_{initial}(\mathbf{r})\; d^3r \tag{3}$$

We focus here on the spatial integral. For Atom-Light interaction, the most important mechanism is the interaction between the electric dipole moment $\vec{\mu}_{el}$ and the electric field $\vec{\mathcal{E}}$ in EM field. Thus, $\hat{H}' = -\vec{\mu}_{el} \cdot \vec{\mathcal{E}} = -\vec{\mu}_{el} \cdot \vec{\mathcal{E}}_0 \cos\omega t$. It follows from Eq. (3) that

$$a_f(t) \propto \left[\int \psi^*_{final}(\mathbf{r})\; \vec{\mu}_{el}\; \psi_{initial}(\mathbf{r})\; d^3r\right] \cdot \vec{\mathcal{E}} \tag{4}$$

The integral $[\ldots]$ in Eq. (4) is key to understand selection rules under the electric dipole mechanism (also called E1 transitions in atomic physics and spectroscopy). It is the "**electric dipole matrix element**", as it is labelled by two indices (the initial and final states).

In the special case of a single electron (e.g. hydrogen atom), $\vec{\mu}_{el} = -e\vec{r}$. A transition from an initial (state 1) to a final state (state 2) occurs with a probability amplitude proportional to a spatial integral given by

$$a_2(t) \propto \overline{\mathbf{r}_{final,initial}} = \int \psi^*_{final}(\mathbf{r})\; \mathbf{r}\; \psi_{initial}(\mathbf{r})\; d^3r\;, \tag{5}$$

where $\mathbf{r} = \vec{r}$. In general, the integral is handled numerically for atoms and molecules. This is the "position matrix element" that determines $a_2(t)$. The probability of a transition from state 1 to state 2 after $\hat{H}'$ is applied for a time t is $|a_2(t)|^2$.

For the hydrogen atom, the integral can be **evaluated analytically**. This integral plays an important role for stimulated processes AND spontaneous emission, as well as setting selection rules. We encountered such integrals in a previous problem on atomic polarizability of the hydrogen atom.

(a) Let's consider transitions in a hydrogen atom. By inspecting the integral

$$a_2(t) \propto \overline{\mathbf{r}_{2s,1s}} \equiv \int \psi_{2s}^*(\mathbf{r})\, \vec{r}\, \psi_{1s}(\mathbf{r})\, d^3r = \int \psi_{200}^*(\mathbf{r})\, \mathbf{r}\, \psi_{100}(\mathbf{r})\, d^3r \tag{6}$$

that would determine a transition between 1s and 2s states, **show that the integral vanishes** and thus the transition is forbidden (not allowed) by the electric dipole mechanism.

(b) For hydrogen atom, the transition between 1s and 2p is allowed. In this case, the integral that matters is

$$a_2(t) \propto \overline{\mathbf{r}_{2p,1s}} \equiv \int \psi_{2p}^*(\mathbf{r})\, \mathbf{r}\, \psi_{1s}(\mathbf{r})\, d^3r \tag{7}$$

Recall that there are several 2p states, labelled by $(n = 2, \ell = 1, m_\ell)$ with $m_\ell = +1, 0, -1$. So let's be concrete. Consider the transition between the 1s ground state and 2p state of $m_\ell = +1$ for which the angular part is $Y_{11}(\theta, \phi)$. Thus, $\psi_{2,1,+1}(\mathbf{r})$ is the final state and $\psi_{1,0,0}(\mathbf{r})$ is the initial state.

(i) In Eq. (7), the integral is a vector because $\mathbf{r}$ is a vector. Explicitly, writing

$$\mathbf{r} = x\hat{x} + y\hat{y} + z\hat{z} = r\sin\theta\cos\phi\; \hat{x} + r\sin\theta\sin\phi\; \hat{y} + r\cos\theta\; \hat{z}\ , \tag{8}$$

evaluate the integral in Eq. (7). It is important to note that the answer is a vector and in general complex. [TA: Give the answer in Bohr radius.]

(ii) For (stimulated) absorption, consider an external field $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$, i.e., the incident light is linearly polarized in z-direction (so the propagating direction is not along z.). The perturbative term in the Hamiltonian $\hat{H}' = -\vec{\mu}_{el} \cdot \vec{\mathcal{E}}$ implies that it is the $\hat{z}$-component of $\overline{\mathbf{r}_{2p,1s}}$ that matters. **Discuss** the condition for the component $z_{2p,1s}$ to be non-zero. Hence, **argue** that such a linearly polarized light *cannot* stimulate an absorption from $\psi_{1,0,0}(\mathbf{r})$ to $\psi_{2,1,+1}(\mathbf{r})$.

(iii) Now consider circularly polarized light. Let the propagation direction be the z-direction. From EM theory, its electric field is on the x-y plane. In particular, a circularly polarized light with its polarization specified by $\mathbf{e}^+ \propto (\hat{x} + i\hat{y})$ has its electric field rotating with time at a fixed point in space (note that there is an time factor $e^{-i\omega t}$ in the field that gives the rotating behavior). Now let's do QM with Eq. (7) for transition from (100) to $(2, 1, +1)$ state. **Show that such a circularly polarized light can stimulate a transition** between $\psi_{1,0,0}(\mathbf{r})$ and $\psi_{2,1,+1}(\mathbf{r})$ by working out Eq. (7).

[Implication: Skillfully manipulating atoms using circularly polarized light can selectively induce transitions and thus put atoms into a particular excited state. For example, techniques in cold atom physics (cooling atoms down to about ∼ 10 nano-Kelvin) also use circularly polarized light to induce selected transitions.]