Quantum Mechanics

August 18, 2022

Work 4 (and only 4) of the 5 problems. Please put each problem solution on a separate sheet of paper and your name on each sheet.

Problem 1

A porphyrin ring is a molecule which is present in chlorophyll, hemoglobin, and other important compounds. Some aspects of the physics of its molecular properties can be described by representing it as a one-dimensional circular path of radius $R = 4\,\text{Å}$, along which 18 electrons are constrained to move.

a.) Write down the normalized one-particle energy eigenfunction of the system, assuming that the electrons do not interact with each other.

b.) How many electrons are there in each level in the ground state of the molecule?

c.) What is the lowest electronic excitation energy of the molecule? What is the corresponding wavelength (give a numerical value) at which the molecule absorbs radiation?

Hint: Compton wavelength of the electron: $\frac{h}{mc} = 0.0242\,\text{Å}$

Problem 2

There are eight possible spin states for a system of three electrons (i.e., $\alpha_1\alpha_2\alpha_3$, $\beta_1\alpha_2\alpha_3$, etc.) Find eight mutually orthogonal linear combinations of these states that are simultaneously eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$, where $\hat{\mathbf{S}} = \hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2 + \hat{\mathbf{s}}_3$ is the total spin operator. What are the eigenvalues of $\hat{S}^2$ and $\hat{S}_z$ for these combinations?

Problem 3

Consider two identical point-like spinless particles of mass M trapped in a large three-dimensional spherical potential well. The total potential of the system can be separated into 3 components that include the well's interaction with each particle and then the interaction between the two particles:

$$V(\vec{r_1}, \vec{r_2}) = \frac{1}{2}M\omega^2\vec{r_1}^2 + \frac{1}{2}M\omega^2\vec{r_2}^2 + \frac{2\hbar^2}{M(\vec{r_1} - \vec{r_2})^2}$$

a.) Determine the Hamiltonian $H(\vec{r_1}, \vec{r_2}) = -\frac{\hbar^2}{2M}(\nabla_1^2 + \nabla_2^2) + V(\vec{r_1}, \vec{r_2})$ for this system in terms of the set of reduced coordinates $\vec{r} = (\vec{r_1} - \vec{r_2})/\sqrt{2}$ and $\vec{R} = (\vec{r_1} + \vec{r_2})/\sqrt{2}$. Separate your Hamiltonian as $H(\vec{r}, \vec{R}) = H(\vec{r}) + H(\vec{R})$.

b.) Determine the ground state wave function and energy for this system. *Hint:* Your $H(\vec{r})$ and $H(\vec{R})$ may look familiar with regards to a particle in a three-dimensional potential well.

c.) How would you expect your wave function to change if the particles are indistinguishable? Also, if we assume the particles have some finite size and are not allowed to overlap, how would this affect the ground state energy? (You do not need to explicitly calculate this, just describe qualitatively how the energy is expected to change and why).

Problem 4

A one-dimensional quantum harmonic oscillator with Hamiltonian

$$\hat{H}_0 = \left(\hat{a}^\dagger \hat{a} + \frac{1}{2}\right)\hbar\omega = \left(\hat{n} + \frac{1}{2}\right)\hbar\omega$$

is subject to a small perturbation $\hat{V} = \lambda \hat{a}^\dagger \hat{a}^\dagger \hat{a}\hat{a}$. Determine the first order perturbative corrections to the energy spectrum. Then, compute the exact solution and compare it with the result of perturbation theory.

Problem 5

Symmetry Transformations in Quantum Mechanics:

a.) *(1 pt.)* Prove that any transformation $\hat{\mathcal{U}}$ which preserves the norm of a quantum state $|\psi\rangle$ in quantum mechanics is **unitary**. That is, show that if

$$|\psi'\rangle \equiv \hat{\mathcal{U}}\,|\psi\rangle \ , \tag{1}$$

with

$$\langle\psi'|\psi'\rangle = \langle\psi|\psi\rangle = 1\,, \tag{2}$$

then

$$\hat{\mathcal{U}}^\dagger\hat{\mathcal{U}} = \hat{\mathbf{1}} \tag{3}$$

with $\hat{\mathbf{1}}$ the identity operator.

b.) *(3 pts.)* Use the **unitary translation operator** to prove that

$$\int_{-\infty}^{\infty} dx\, e^{-ikx}\ \langle p|\ \hat{\mathcal{O}}(x)\,\hat{\mathcal{O}}(0)\,|p\rangle = 2\pi\hbar\ \Big|\langle p|\ \hat{\mathcal{O}}(0)\,|p-\hbar k\rangle\Big|^2\ , \tag{4}$$

where the $|p\rangle$ is a momentum eigenstate and $\hat{\mathcal{O}}(x)$ is a quantum operator that depends on the position x. Here we are working in one spatial dimension for simplicity. You will need the completeness relation

$$\int_{-\infty}^{\infty} dp\ |p\rangle\,\langle p| = \hat{\mathbf{1}} \tag{5}$$

for momentum eigenstates $|p\rangle$.

c.) *(3 pts.)* The nuclear spin of a proton (a spin-1/2 particle) is initially in the spin-up state $|\psi\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$. An NMR machine delivers a pulsed magnetic field which rotates the nuclear spin by an angle of $\pi/2$ radians counterclockwise about the axis $\hat{n} = \frac{1}{\sqrt{2}}(-\hat{\imath} + \hat{\jmath})$ with $\hat{\imath}, \hat{\jmath}$ unit vectors along the x- and y-axes. Use the **unitary rotation operator** to find the quantum state of the proton spin after the pulse. You will need the identity

$$\exp\Big\{-i\theta\,\Big[\,\vec{\sigma}\,\Big]\cdot\hat{n}\Big\} = \cos\theta\,\Big[\,\hat{\mathbf{1}}\,\Big] - i\sin\theta\Big[\,\vec{\sigma}\,\Big]\cdot\hat{n} \tag{6}$$

for the Pauli matrices

$$\Big[\,\sigma_x\Big] = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad , \quad \Big[\,\sigma_y\Big] = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad , \quad \Big[\,\sigma_z\Big] = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad . \tag{7}$$

d.) *(3 pts.)* A qubit is engineered to have two quantum states: a ground state denoted $|0\rangle$ with energy ε, and an excited state denoted $|1\rangle$ with energy 3ε. The qubit is initially prepared at time $t = 0$ in the superposition state

$$|\psi(0)\rangle = \sqrt{\frac{2}{3}}\,|0\rangle - \sqrt{\frac{1}{3}}\,|1\rangle \ . \tag{8}$$

Use the **unitary time-evolution operator** to predict what the state of the qubit will be at the later time $t = \pi\hbar/2\varepsilon$.