CHM 428 Assignment 4

April 22, 2024

1. The operator corresponding to counterclockwise rotation of a system by an infinitesimal angle $\delta\phi$ about a unit vector $\tilde{n}$ is given by $\hat{D}(\tilde{n}, \delta\phi) = 1 - i\frac{\delta\phi}{\hbar}\hat{\vec{J}} \cdot \tilde{n}$. Show that the components of the angular momentum $\hat{\vec{J}}$ satisfy the commutation relations $\left[\hat{J}_\alpha, \hat{J}_\beta\right] = i\hbar\epsilon_{\alpha,\beta,\gamma}\hat{J}_\gamma$.

2. Write down the probability current density operator (a) in polar coordinates for a 2-d system, and (b) in spherical coordinates for a 3-d system. Show that for a particle constrained to move an a ring of radius R, the current operator commutes with the Hamiltonian and can be used to resolve degeneracies.

3. An object is in an angular momentum state $j = 1$. For this state derive the matrix representation of $\hat{J}_x$, $\hat{J}_y$, $\hat{J}_z$, $\hat{J}^+$ and $\hat{J}^-$ in the J_z basis.

4. (a) How do the spherical polar coordinates of a point (r, θ, ϕ) transform under inversion about the origin?

   (b) The associated Legendre polynomials are defined below in equation 1. Show that $P_l^{-m} = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m$ and that $P_l^m(-x) = (-1)^{(l+m)} P_l^m(x)$.

   (c) Using the definition of the spherical harmonics in equation 2 show that $Y_l^m(-\tilde{\mathbf{r}}) = (-1)^l Y_l^m(\tilde{\mathbf{r}})$, where $\tilde{\mathbf{r}}$ is the unit vector along a position vector specified by the angles θ and ϕ.

5. Derive radial Schrödinger equations (by method of separation of variables) involving a particle of mass μ moving under the potential $V(\vec{r})$ given by

(a) $V(r) = \frac{C}{r}$

(b) $V(r) = Cr^2$

(c) $V(r) = 0$ when $r < R$ but $V(r) = \infty$ if $r > R$ (in 2-dimensions).

(d) $V(r) = 0$ when $r < R$ but $V(r) = \infty$ if $r > R$ (in 3-dimensions).

Here C is a constant and $r = |\vec{r}|$.

6. Consider an object in an angular momentum eigenstate $|j, m_j\rangle$ where $j = \frac{1}{2}$.

   (a) What are the possible m_j values corresponding to eigenstates of $\hat{J}_z$?

   (b) Write down the operators $\hat{J}^2$, $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ as matrices in the basis of the $|j, m_j\rangle$ states.

   (c) If the object is in a state $|\psi\rangle = \frac{1}{\sqrt{2}} \left(|\frac{1}{2}, \frac{1}{2}\rangle + |\frac{1}{2}, -\frac{1}{2}\rangle \right)$ calculate the expectation value of $\hat{J}_x$ and $\hat{J}_y$ in the state.

7. An object with angular moment quantum number $j = \frac{1}{2}$ is place under a magnetic field, $\vec{B} = B\hat{k}$, and is described by the Hamiltonian,

$$\hat{H} = \hat{H}_0 + \lambda \hat{\vec{J}} \cdot \vec{B}$$

   where $\hat{H}_0 = \frac{\hat{J}^2}{2I}$ and λ and I are real, positive constants.

   (a) What are the eigenstates and eigenvalues of $\hat{H}_0$? Are there any degeneracies?

   (b) What variables are conserved in the presence of the magnetic field?

   (c) What would happen to the degeneracies in the system in the presence of the magnetic field? What would be the new energies?

   (d) If the system is in the new ground state at $t = 0$, then at what rate do the expectation values of $\hat{J}_x$ and $\hat{J}_y$ change?

8. Given the angular wavefunctions possible for the hydrogen atom for $l = 0, 1, 2$, derive real wavefunctions from these that are still eigenfunctions of $\hat{L}^2$ operator. For each real combination comment on the transformation properties under rotation.

9. Apply the angular momentum operator in the x-direction to the following functions:

   (a) $\frac{5\pi}{4} + 7\exp(\pi^2)$

   (b) $4\pi\sin(\theta)$

   (c) $\frac{3}{2}\cos(\theta)\exp(i\theta)$

10. Calculate the reduced mass of HCl molecule given that the mass of H atom is 1.0078 amu and the mass of Cl atom is 34.9688 amu. Note that 1 amu = $1.660565*10^{-27}$ kg. Given the equilibrium bond-length of HCl is 1.275Å, calculate the rotational constant associated with rotational motion of HCl.

11. $^{79}Br^{79}Br$ has a force constant of 240 N/m . Given this information:

    (a) Calculate the fundamental vibrational frequency, and

    (b) Calculate the $^{79}Br^{79}Br$ zero point energy.

12. Using the definitions for $\hat{L}_z$ compute its expectation value for a $2p_x$ and a $2p_y$ orbital in the hydrogen atom. Are these states eigenstates of $\hat{L}_z$? How about $\hat{L^2}$?

13. Find the reduced mass of an electron in a Tritium atom. Set the mass of the Tritium to be 5.008267×10^{-27} kg . Then find the value of the Rydberg constant for the Tritium atom.

14. Compute the expectation value of r of an electron (distance from nucleus) when it is in the $1s$ orbital of a H-atom. How does this value change when we consider the same orbital in He^+ ion?

15. Calculate the Rydberg constant for a deuterium atom and atomic hydrogen given the reduced mass of a deuterium atom is 9.106909×10^{-31}kg and the reduced mass of hydrogen is 9.104431×10^{-31}kg . Compare both of these answers with the experimental result (109677.6cm^{-1}). Then determine the ratio of the frequencies of the lines in the spectra of atomic hydrogen and atomic deuterium.

16. Among the following molecules which ones will show vibrational absorption spectra? (a) CO, (b) N_2, (c) HBr, (d) F_2. Justify your answer.

17. Why does a molecule need to possess a non-zero dipole moment to be able to absorb light and get rotationally excited?

Useful Formulae:

$$P_l^m(x) = \frac{(-1)^m}{2^l l!}(1-x^2)^{\frac{m}{2}} \frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l \tag{1}$$

$$Y_l^m(\theta,\phi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(\cos\theta) \mathrm{e}^{im\phi} \tag{2}$$

$$\tag{3}$$