Quantum Mechanics of Atoms and Molecules (PC3602)
Exercise 2

1. A particle has spin quantum number $s = 1$.
(a) What are the eigenvalues of $\hat{S}_z$?
(b) Using the eigenstates of $\hat{S}_z$ as basis, determine in matrix form its operators $\hat{S}_z$, and $\hat{S}^{\pm}$.
(c) Determine the eigenvalues and eigenstates of $\hat{S}_y$.

2. (a) Prove any one of the following three commutation relationships

$$\left[\hat{L}_x,\ \hat{L}_y\right] = i\hbar\hat{L}_z, \quad \left[\hat{L}_y,\ \hat{L}_z\right] = i\hbar\hat{L}_x, \quad \left[\hat{L}_z,\ \hat{L}_x\right] = i\hbar\hat{L}_y\ .$$

(b) Use (a) to prove

$$\left[\hat{L}_z,\ \hat{L}^{\pm}\right] = \pm\hbar\hat{L}^{\pm}, \quad \left[\hat{L}^{+},\ \hat{L}^{-}\right] = 2\hbar\hat{L}_z$$

where $\hat{L}^{\pm} = \hat{L}_x \pm i\hat{L}_y$ are defined as raising and lowering operators for angular momentum.
(c) Prove

$$\hat{L}^{+}\hat{L}^{-} = \hat{L}^2 - \hat{L}_z^2 + \hbar\hat{L}_z, \quad \hat{L}^{-}\hat{L}^{+} = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z$$

where $\hat{L}^2 = \hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$.

3. (a) Prove the following commutation relationships

$$\begin{aligned}\left[\hat{L}^2,\ \hat{L}_1^2\right] &= \left[\hat{L}^2,\ \hat{L}_2^2\right] = \left[\hat{L}^2,\ \hat{L}_z\right] = 0 \\ \left[\hat{L}_z,\ \hat{L}_1^2\right] &= \left[\hat{L}_z,\ \hat{L}_2^2\right] = 0\end{aligned}$$

where $\hat{\mathbf{L}} = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2$ is the total angular momentum, $\hat{L}_z = \hat{L}_{z1} + \hat{L}_{z2}$ is its z-component, and we have assumed $\left[\hat{L}_1^2,\ \hat{L}_2^2\right] = 0$. Hence the good quantum numbers for the eigenstates of $\hat{L}^2$ are (l_1, l_2, l, m), i.e., the corresponding quantum numbers of the operators $\hat{L}_1^2, \hat{L}_2^2, \hat{L}^2$ and $\hat{L}_z$.
(b) Apply angular momentum addition theorem to obtain all eigenvalues of the following Hamiltonian

$$H = \hat{\mathbf{L}}_1 \cdot \hat{\mathbf{L}}_2 + \alpha\hat{L}_z$$

where α is a constant, $\hat{L}_z = \hat{L}_{z1} + \hat{L}_{z2}$ and the angular momentum quantum numbers of $\hat{\mathbf{L}}_1$ and $\hat{\mathbf{L}}_2$ are $l_1 = 1$ and $l_2 = 3/2$ respectively. Hint: use $\hat{\mathbf{L}}^2 = \hat{\mathbf{L}}_1^2 + \hat{\mathbf{L}}_2^2 + 2\hat{\mathbf{L}}_1 \cdot \hat{\mathbf{L}}_2$.

4. Two interacting spins (both with $s = 1/2$) have the following Hamiltonian

$$\hat{H} = \alpha \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 \ ,$$

where α is the coupling constant.
(a) Show that

$$\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \frac{1}{2}\left(\hat{S}_1^+ \hat{S}_2^- + \hat{S}_1^- \hat{S}_2^+\right) + \hat{S}_1^z \hat{S}_2^z \ .$$

(b) Use Angular Momentum Addition Theorem to determine its eigenvalues and their degeneracies.
(c) Determine the corresponding eigenstates in terms of the single-spin states $|\uparrow\rangle$ and $|\downarrow\rangle$. Hint: Use results of Part (b) to construct four different two-spin states in terms of one-spin states $|\uparrow\rangle$ and $|\downarrow\rangle$ and use Part (a) to prove that they are indeed eigenstates of $\hat{H}$.

5. (a) State the complete Hund's rules.
(b). Write down electron configuration of boron and derive its atomic terms. Which one corresponds to its ground state?
(c) Repeat Part (b) for Carbon.

6. Consider a quantum system of two identical particles. In the independent-particle approximation, given n single-particle states $[\phi_i(x), i = 1, 2, \cdots, n; n \geq 2]$, prove that there are $n(n-1)/2$ possible antisymmetric states and $n(n+1)/2$ symmetric states for the two-particle system. [Note: In proving this theorem, you may as well construct all theses states, starting with $n = 2, 3$, etc., then extending to general n and proving it by induction.]