Quantum Mechanics of Atoms and Molecules (PC 3602)
Exercise 4

1. (a) The time-dependent Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}(t)$ with

$$\hat{H}_0 = \frac{eB_0}{m}\hat{S}_z, \quad \hat{V}(t) = \frac{eB_1}{m}\left(\hat{S}_x \cos\omega t + \hat{S}_y \sin\omega t\right)$$

describes a spin $S = 1/2$ system which is subject to the static magnetic field $(0, 0, B_0)$ and the rotating magnetic field $(B_1 \cos\omega t, B_1 \sin\omega t, 0)$. B_0 and B_1 are uniform throughout space. Initially, at time $t = 0$, the spin of the system is pointing in the direction of the negative z-axis. Assuming B_1 is weak and taking $\hat{V}(t)$ as perturbation, calculate the probability that at time $t > 0$ the spin points in the positive z-axis.
(b) Discuss at what value of ω, the perturbation theory breaks down for sufficiently large t, however weak B_1. Suggest a criterion in t for the perturbation theory to hold.

2. The spin interaction energy of positronium in a magnetic field can be written as a (4×4) matrix Hamiltonian

$$\hat{H} = \begin{pmatrix} \varepsilon_1 & v & 0 & 0 \\ v & \varepsilon_2 & 0 & 0 \\ 0 & 0 & \varepsilon_3 & 0 \\ 0 & 0 & 0 & \varepsilon_4 \end{pmatrix}.$$

Calculate all eigenvalues of $\hat{H}$ exactly. Compare the perturbation results of Exercise 3.2 for the energies with the corresponding exact energies under the conditions that $\varepsilon_1 < \varepsilon_2$ and $v \ll \varepsilon_2 - \varepsilon_1$.

3. In H_2^+ problem, using molecular orbitals as linear combination of two hydrogen atomic ground-state orbitals ϕ_a and ϕ_b, i.e., $\psi = c_a\phi_a + c_b\phi_b$, we derive the matrix equation

$$\begin{pmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0\,,$$

where three integrals are defined as $\alpha = \langle\phi_a|\hat{H}|\phi_a\rangle$, $\beta = \langle\phi_a|\hat{H}|\phi_b\rangle$ and $S = \langle\phi_a|\phi_b\rangle$.
(a) Determine energy E and molecular wavefunction coefficients c_a and c_b in terms of α, β and S.
(b) The above matrix equation holds for a homonuclear diatomic molecule. Write down similar equation for a heteronuclear molecule. Explain any integral you may use. Determine the energy E in terms of these integrals.

4. (a) Write down the ground-state electron term of H_2 molecule.
(b) Write down the corresponding ground-state wavefunction and explain each notation you use.

5. (a) Write down the ground-state electron configuration of Li_2, Be_2 and N_2, using molecule orbitals discussed in class.
(b) By counting the bond order of these configurations, determine which molecules is unstable and which molecule is stable. Derive the ground-state molecular term of the stable molecules.