5.80 Small-Molecule Spectroscopy and Dynamics
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Problem Set #2

1. The number of possible spin eigenfunctions for a single particle of spin I is $2I + 1$.

   (a) How many linearly independent spin eigenfunctions are possible for two equivalent particles of spin I?

   (b) For a particle with $I = 1$, denote the three spin eigenfunctions by α, β, and γ, corresponding to the eigenvalues $M_z = +, 0, -$. How many linearly independent symmetric and how many linearly independent antisymmetric spin states are there for two equivalent particles with $I = 1$?

2. Atomic eigenfunctions contain a factor $\exp(iM\phi)$. When the atom is a magnetic field B, the quantum number M represents the projection of the J–vector on B ($-J \leq M \leq +J$). The usual selection rules for L, S, and J still hold for moderate B, and in addition a selection rule governing the values of ΔM becomes important. The dipole-moment operators for transitions involving M are $ce\epsilon_{||}$ and $c'e\epsilon_{\perp}\cos\phi$. The coefficients c and c' are non-zero constants (for the purposes of this problem); e is the charge on the electron; and $\epsilon_{||}$ and $\epsilon_{\perp}$ are the components of the electric field of the radiation parallel and perpendicular to B. Derive the selection rules for ΔM for radiation polarized parallel and perpendicular to B.

3. Calculate the Zeeman pattern to be expected for the sodium *D*–lines at 10,000 Gauss (*G*). You may neglect nuclear hyperfine interactions. Indicate the polarization of each Zeeman line, that is, whether the electric vector of the emitted radiation is parallel to the applied magnetic field (π–component) or perpendicular to it (σ–component).

   (a) Show qualitatively the Stark effect to be expected for the sodium *D*–lines. The splittings are proportional to what power of the electric field strength?

(b) What do you think might happen to a beam of ground-state sodium atoms passing through a strong inhomogeneous magnetic field? a strong inhomogeneous electric field?

4. An atom is in a $(3d)^2\ {}^3P_0$ state.

(a) List all L−S−J terms to which an electric dipole allowed transition might occur.

(b) List all two-electron configurations into which electric dipole allowed transitions can occur from $(3d)^2$ ${}^3P_0$.

5. The "transition moment," or the probability of transition, between two rotational levels in a linear molecule may be assumed to depend only on the permanent electric dipole moment of the molecule and thus to be the same for all allowed pure-rotational transitions. In the pure-rotational *emission spectrum* of $H^{35}Cl$ gas, lines at 106.0 cm^{-1} and 233.2 cm^{-1} are observed to have equal intensities. What is the temperature of the gas? The rotational constant B for $H^{35}Cl$ is known to be 10.6 cm^{-1}, and the ratio hc/k has the value 1.44 cm·K.

6. What would happen to the Birge-Sponer extrapolation scheme for a molecular potential that correlates with ionic states of the separated atoms?