1.1 Use Table 1.3 and Fig. 1.3 in Tables-I to convince yourself that T_d is the symmetry group of the methane molecule.

1.2 **a)** Construct explicitly the six matrices for the vector representation of C_{3v}. *Hint:* Remember that the *nth* column of a transformation matrix coincides with the transformed of the *nth* basis vector.

b) Construct explicitly the matrices of the vector representation of T_d for the group elements C_{31}^{+}, C_{2y}, σ_{dc} and S_{4z}^{+}.

1.3 Show that a mirror reflection σ_z can be obtained as the product of a C_{2z} rotation perpendicular to the mirror by an inversion.

2.1 **a)** Use the general formulas for the characters of the rotational representation to show that $R = A_2 + E$ for the point group C_{3v}.

b) Construct the six matrices for the rotational representation of C_{3v}. Check your result with the general formulas for the characters.

2.2 For the CH_4 molecule with symmetry group T_d, construct explicitly the mechanical representation matrices $M(C_{31}^{+})$, $M(C_{2y})$ and $M(\sigma_{df})$.

2.3 Boron trifluoride (BF_3) is a planar molecule with the three fluorine atoms at the vertices of an equilateral triangle and the boron atom at the center.

a) Identify the point group for this molecule.

b) Obtain the decomposition of the vector and rotational representations.

c) Obtain the decomposition of the vibrational representation and describe qualitatively the spectrum.

3.1 For the deuterated methane molecule CH_3D with symmetry group C_{3v}

a) Obtain the form of the potential matrix in symmetry-adapted coordinates. Indicate clearly the ordering used.

b) Exhibit the block structure of the matrices of the vibrational representation $Vib(g)$. Should we use the same order as in the previous question?

3.2 Do the same for the boron trifluoride (BF_3) molecule.

4.1 **a)** Show that the group of symmetry of the ammonia molecule (NH_3) is a subgroup of the one for boron trifluoride (BF_3).

b) Use subduction to obtain the decomposition of the vibrational representation for ammonia. Give a qualitative description of the spectrum of vibrations of NH_3.

4.2 Consider electrons in orbitals around the carbon and hydrogen atoms in a methane (CH_4) molecule. The corresponding orbitals will be affected by the local molecular field. In this exercise we neglect the spin-orbit interaction.

a) Obtain the splitting of p and d orbitals at the carbon atom

b) Do the same for orbitals at a hydrogen atom.

4.3 Obtain the splitting of p and d orbitals due to a crystal field with local T_h symmetry in the presence of a strong spin-orbit interaction.

5.1 Check the correctness of the little groups assigned in the slides to the symmetry points and lines of the first Brillouin zone. Be careful to identify the reciprocal lattice vectors that go with each transformation.

5.2 Obtain the phases at the K-point. Note that you have to compute phases only for transformations that belong to the site symmetry group, since otherwise they don't contribute to the character.

5.3 In this exercise you will extend the analysis in the slides to the bands arising from the (p_x, p_y) orbitals. Now there will be four bands instead of two.

a) Show that at the symmetry points

$$T_\Gamma = \Gamma_5 + \Gamma_6\,,\;\; T_K = K_1 + K_2 + K_3\,,\;\; T_M = M_1 + M_2 + M_3 + M_4$$

b) Use subduction to show that at the symmetry lines

$$T_T = 2\,T_1 + 2\,T_2\,,\;\; T_\Sigma = 2\Sigma_1 + 2\Sigma_2\,,\;\; T_{T'} = 2\,T_1' + 2\,T_2'$$

c) Sketch a few possibilities for the bands. You will find that in some cases the four bands are interconnected, while in others they form two disconnected sets.

Hint: For question a) you can repeat the analysis in the slides, just substitute $\chi_E(g)$ for $\chi_{A_1}(g)$ in the formula for the character. To do question b) you will also have to extend the compatibility relations to some IRs not considered in the slides.

5.4 In this exercise you will analyze the bands arising from *spinful* electrons in p_z orbitals. You will also have four bands (two atoms $\times$ two spin states).

a) Show that electron spin belongs to the IR $\bar{E}_1$ of the site symmetry double group $\bar{C}_{3v}$.

b) Show that at the symmetry points

$$T_\Gamma = \Gamma_7 + \Gamma_8\,,\;\; T_K = K_4 + K_5 + K_6\,,\;\; T_M = 2\,M_5$$

c) Use subduction to show that at the symmetry lines

$$T_T = 2\,T_3 + 2\,T_4\,,\;\; T_\Sigma = 2\Sigma_3 + 2\Sigma_4\,,\;\; T_{T'} = 2\,T_3' + 2\,T_4'$$

d) Sketch a few possibilities for the bands. As in problem 5.4, there are cases where the four bands are interconnected, while in others they form two disconnected sets.