Physically based extended problems

The following problems are based upon processes required in the interpreting and processing of AIMPRO based computed data to make connections with experimental data.

1) The hyperfine interaction tensor is a rank-two tensor connecting the electronic spin and the nuclear spin in the spin-Hamiltonian. As calculated, in general the raw tensor contains nine values that are referenced to the cubic axes of the Cartesian space occupied by the system,

$$\begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix},$$

but this is not the form normally expressed in experiment. Instead, the diagonal form is determined, which can be viewed as being the eigenvalues and eigenvectors of this matrix. For a typical, non-cubic paramagnetic centre in solid solution, there are equally populated orientations with respect to the lattice. This means that the tensor desired for inclusion in a report, or with reference to a published orientation, may differ from that evaluated in the hyperfine analysis. In addition, where the defect can rapidly reorient between different orientations on the time-scale of the EPR experiment, the average of the tensors for the different orientations must be diagonalised in order to determine the motionally averaged principal values and directions of the hyperfine tensor. The following is the raw hyperfine tensor for the one orientation of a defect in diamond in units of 10^8 Hz to six significant figures:

$$\begin{pmatrix} 0.828445 & 0.127174 & -0.124806 \\ 0.127174 & 0.833009 & -0.127175 \\ -0.124806 & -0.127175 & 0.828446 \end{pmatrix}.$$

   a) Confirm that the eigenvalues are approximately 70, 70 and 108 MHz, and determine the normalised eigenvalues for each eigenvector.
   b) Based upon the directions and the degeneracies of the values, or otherwise, determine the symmetry of the defect.
   c) Find the raw hyperfine tensor for the orientation of the defect generated by reflection in the $(10\bar{1})$ plane, and the average generated by combining the two tensors.
   d) Calculate the eigenvalues and eigenvectors of the average tensor.
   e) What is the symmetry of the motionally averaged system?

2) A student is starting a new project, and needs to build a model of GaN in the Wurtzite crystal phase.
   a) Locate sufficient information in the literature, and generate the unit cell of GaN sufficient to completely specify the positions of the atoms in the basis and the corresponding Cartesian lattice vectors.
   b) In terms of the primitive lattice vectors as specified in part a), generate a non-primitive cell with orthogonal lattice vectors containing eight atoms.
   c) For the project, the supercell required must have a lattice vector pointing in the $[1\bar{1}01]$ direction in terms of the conventional notation for a hexagonal lattice. What is the minimum volume of a cell satisfying this condition as a multiple of the primitive cell volume?

d) If the c-axis is parallel to the Cartesian direction $\vec{\imath} + \vec{\jmath} + \vec{k}$, what are the three primitive lattice vectors of the Wurtzite structure?

3) The band-structure is needed for a defect system in a 2744 atom cubic supercell of diamond. The calculation is needed so that the dispersion in a narrowly split electronic doublet can be determined, relating to a Jahn-Teller distortion from trigonal to a monoclinic centre with a (110) mirror plane. In addition, the corresponding band-structure for the defect free cell of the same size and shape is needed.
   a) Suggest a contiguous path through the irreducible part of the Brillouin-zone made up of at least five symmetrically non-equivalent branches. Include a Γ-R branch and a branch passing through the X-point amongst your selections. [Hint: is there more than one Γ-R branch?]
   b) The evaluation of the band-structure in such a large system with so many branches is likely to be a computationally costly procedure. However, the corresponding bands of the 2744 atom bulk cell may be found without approximation by calculating a band-structure in a two atom cell, since all of the properties of perfect bulk diamond are in principle contained within the primitive lattice. Describe in detail how in practice one might realise the band-structure for the 2744 atom cell using the primitive cell.
   c) Would the procedure be simpler using the conventional unit cell in this case? Explain your answer. [Hint: it may help to express the 2744 atom cell in terms of multiples of the conventional cell.]
   d) Would either b) or c) result in a faster evaluation of the bands for the pure 2744 atom cell relative to performing it directly? Again, explain your answer fully.

4) A compound material, such as $SrTiO_3$ (STO), is thermodynamically stable only under conditions where it has a lower free energy than any other combination of materials made up from the same constituents. For example, under some conditions it may be more favourable to form Sr and Ti metals and oxygen gas. This may be expressed in terms of the atomic chemical potentials, μ_{Sr}, μ_{Ti} and μ_O.
   a) Examine the literature to determine the most likely materials made up from these three species. [Hint: there are at least seven of them.]
   b) Assuming it is possible to determine the energies of each system, propose a method for determining the ranges of values of the three chemical potentials for which STO is the equilibrium phase.
   c) How might the process be generalised to systems such as $Ba_xSr_{1-x}TiO_3$ (BST) involving four species?
   d) How do the chemical potentials of the species depend upon temperature?
   e) What is the role of the electron chemical potential in these materials? Make sure that you comment upon the impact of temperature in your answer.