AIMPRO basics test

Answer the following questions on the underpinning physical and computational theory relating to the use of AIMPRO, and its use in the modeling of systems of atoms, both molecular and crystalline.

1. What term in the total energy does the choice of LDA or GGA functional chiefly relate to?
2. Write down the mathematical form of a plain Gausian, s-type orbital as used in AIMPRO.
3. How does size of the exponent as written in the `hgh-pots` file affect the shape of the function?
4. How is the s-type function modified to express higher orbital angular momentum?
5. Rank the order of the contribution of uncertainty in a total energy of a structurally optimized molecule, simulated by placing it in a periodic boundary condition:
    a. Cell size
    b. Functional
    c. Wave function basis
    d. Pseudo potential type (HGH, TM, BHS, Vanderbilt, …)
    e. Plane wave basis
    f. Electronic temperature
    g. Optimization method (`diis`, `cong`, `cubic2`, …)
    h. Sampling density
    i. Cell shape
    j. Starting structure
    k. Symmetry
    l. Self-consistency tolerance
    m. Units in which the structure is specified
    n. The division of the electrons between the core and the valence (e.g. Na could be just the single $3s$ electron, termed a valence set, or the $2s + 2p$ and the $3s$ electrons, termed a semi-core set).
    o. The charge density fitting basis (`cdbas`)
    p. The number of nodes you use
    q. The use of filtration
6. In pseudo potential theory, what does ‘norm conserving’ mean?
7. Give an example of a system for which the Born-Oppenheimer approximation is invalid.
8. What key term in the total energy is missing in a standard Hartree-Fock calculation? How is this term accounted for in a ‘CI’ method?
9. How many vibrational modes does a non-linear molecule containing N atoms have? How many does a crystal with N atoms have? How many normal modes does a ‘`derivs{all}`’ run generate for a system of N atoms yield, and why does this differ from the values of the number of vibrational modes?

10. In AIMPRO, the ‘filling’ option contains the energy term kT. If no other filling options are selected, what does this energy represent? How does the choice of temperature affect the calculation in terms of:
    a. The electronic structure
    b. The total energy

    Indicate in your answer both qualitatively and quantitatively.
11. Outline the meaning of the ‘conjugate gradients’ algorithm, and explain how it is used in the context of structural optimization. Ensure that you have included **all** stages in a single optimization step.
12. Explain the difference between the Helmholtz and Gibbs functions (free energies). By default, which type of energy is obtained in AIMPRO?
13. Normally, the atom cores are at zero temperature in an AIMPRO calculation. Explain the meaning of the term ‘zero point energy’ and explain how it may be justified that this term is not routinely included in the use of total energies obtained using AIMPRO.
14. Explain the expression ‘self consistent’ in the context of the energies obtained in an AIMPRO calculation. Is it important that we use self-consistent energies? Explain why or why-not.
15. Density functional methods usually yield Kohn-Sham energies and functions that are interpreted as one-electron energies and wave functions. Is such an interpretation valid? Explain your answer.
16. Outline Koopman’s and Janek’s theorems. Can they be applied to an AIMPRO calculation?
17. Vibrational modes obtained with AIMPRO are usually ‘quasi-harmonic’ in nature.
    a. By explaining how the second-derivative of energy with respect to nuclear displacement can be used to determine vibrational frequencies, i.e. explaining the dynamical matrix, justify the use of the term ‘harmonic’.
    b. Explain why in practice the ‘quasi’ epithet is required. Under what circumstances is the harmonic approximation least accurate?
    c. Give an example of a system for which the harmonic frequency deviates from the true frequency to a significant degree.
18. Outline the advantages and disadvantages of using pseudo potentials.
19. Explain why it may not be possible to use AIMPRO to determine the ground state energy of an oxygen atom, even if all numerical and computational parameters, such as the basis, functional and pseudo potentials are **perfect**.
20. Explain the difference between `int-c` and `int-p` structure specifications.