List of example questions that could come up on the oral exam

The answer to these questions should should only be a couple of sentences.

1. Explain what is meant by Hartree-Fock in one or two sentences.

2. What is a Slater determinant?

3. How does the contribution to the energy of an electron pair with same spin differ from that of an electron pair with opposite spin?

4. Why is the ground state of an O_2 molecule a triplet state?

5. What is the difference between a bonding and an anti-bonding molecular orbital?

6. Why is it important to use exactly the same level of theory (approximation to the wave function and basis set) for both the molecule and the individual atoms when the bond energy of a molecule is calculated?

7. What is the energy unit Hartree and how does it compare with electron volts and kJ/mol?

8. Explain what is meant by a variational calculation.

9. Why must the energy decrease or stay the same when more basis functions are included in a variational calculation?

10. Why is there no variational principle for bond energy?

11. How can relative electronegativity be deduced from calculated electron density?

12. What is meant by spin multiplicity (give some examples)?

13. Will a basis set that has a larger number of basis functions always give a lower energy than a basis set that has smaller number of basis functions?

14. What is the difference between a restricted and unrestricted Hartree-Fock calculation?

15. Why does the RHF energy of an H_2 molecule not reach the energy of two isolated H-atoms when the bond length increases?

16. What is required to get the right dissociation limit for an H_2 molecule in a calculation that is based on restricted Slater determinants?

17. Why does UHF give the right dissociation limit for H_2?

18. What is the disadvantage of UHF calculations as compared with RHF calculations?

19. Explain what is meant by the STO-3G, 3-21G and 6-31G basis sets.

20. How do the 6-311G* and 6-311G** basis sets compare with the 6-311G basis set?

21. What is the difference between a double zeta and a triple zeta basis set?

22. Describe how a 'electrostatic potential map' of electron density is constructed and what information it can convey.

23. How could an electrostatic potential map be used to predict reaction mechanism?

24. What is meant by the 'Hartree-Fock limit'?

25. Why is the ground electronic state of the methylene molecule a triplet?

26. Compare the bond angle of the singlet and triplet states of methylene and explain why it is larger for one than the other.

27. Why is a Hartree-Fock estimate of the singlet-triplet energy gap typically not accurate?

28. What is meant by a configuration interaction (CI) calculation and how is it performed?

29. What is meant by a QCISD calculation?

30. What is meant by a QCISD(T) calculation?

31. Why is the C-C bond in the excited state of ethene longer than in the ground state?

32. What is meant by a semi-empirical calculation, and why do such calculations sometimes give better results than Hartree-Fock calculations?

33. What is meant by MP calculations of electronic structure?

34. What is an MP2 calculation and how does it compare with an MP4 calculation?

35. What is the difference between a restricted and an unrestricted MP2 calculation?

36. How do MP2 results compare in accuracy with HF and CISD(T) results?

37. Why is MP2 often used in calculations of the binding energy in molecular clusters?

38. What is meant by size consistency?

39. How does the boiling point of a liquid correlate with the strength of the interaction between the molecules of the liquid?

40. What is meant by density functional theory of electronic structure?

41. What does the Hohenberg-Kohn theorem state?

42. What is meant by a Kohn-Sham energy functional?

43. For what properties are DFT calculations known to give accurate predictions and for what are DFT calculations known to be inaccurate?

44. What are the main categories of energy functionals, how do they differ and what is their relative accuracy typically?

45. Can a variational calculation using a DFT functional give a lower energy than the exact energy?

46. What is meant by self-interaction error in DFT calculations?

47. What is the difference between the BLYP and B3LYP functionals?

48. What is Mulliken population analysis?

49. Why is Mulliken population analysis not mathematically sound?

50. When the C-F bond in fluoromethane is stretched, UHF gives more accurate results than DFT. Why is that?

51. What is mean by a vibrational normal mode?

52. How many vibrational modes does a molecule with N atoms have?

53. How do vibrational frequencies calculated with HF usually compare with experimental values?

54. What is meant by anharmonicity and what effect does it have on calculated frequencies and IR spectrum?

55. What is transition state theory (TST) and what are the four assumptions it is based on?

56. Which assumtion in TST is typically weakest?

57. What is meant by the 'minimum energy path' of a transition?

58. What is meant by the 'nudged elastic band method (NEB)'?

59. What is meant by a transition state dividing surface?

60. Often, saddle points are referred to as transition states. Why is that strictly not correct?

61. What is meant by a reaction coordinate and give an example of a good choice for a reaction coordinate?

62. What is meant by the harmonic approximation to transition state theory?

63. What is the thermal energy at room temperature?