

4. A typical carbon-carbon single bond is 1.4 Å. How many meters is that?

5. The Hamiltonian for a molecule is given by

$$\hat{\mathcal{H}} = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_k \frac{1}{2} \nabla_k^2 - \sum_i \sum_k \frac{Z_k}{r_{ik}} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{k<l} \frac{Z_k Z_l}{r_{kl}}$$

in atomic units.

(a) What is the meaning of each of the five terms?

(b) Why are the sums in the last two terms $\sum_{i<j}$ and $\sum_{k<l}$ rather than $\sum_i \sum_j$ and $\sum_k \sum_l$?

6. In your own words, describe the Born-Oppenheimer approximation and its importance to computational chemistry. Also, give a situation where the Born-Oppenheimer approximation may lead to significant error in a calculation.

7. The solution to the equation $\hat{\mathcal{H}}\Psi = E\Psi$ for multielectron systems is complicated by the fact that Hamiltonian (especially the electron-electron interaction) depends on the wavefunction. Explain how the self-consistent field procedure overcomes this issue.

8. What is the connection between the Pauli Exclusion Principle and the use of Slater determinants to express electronic wavefunctions?
9. Atomic orbitals are not Gaussians. Atomic orbitals have a cusp at the nucleus, Gaussians do not. Atomic orbitals go to zero like e^{-r} as $r \rightarrow \infty$, Gaussians go to zero like e^{-r^2} as $r \rightarrow \infty$. Why then are Gaussian basis functions used in so many electronic structure calculations? How do Gaussian basis sets address these deficiencies?
10. What is the advantage of a split-valence double-zeta basis set over a full double-zeta basis set?

15. Write down all of the calculations one would have to perform to compute the enthalpy of a molecule using the MP2/6-311+G(2df,2p)//HF/6-31+G(d,p) model chemistry.
16. What is the advantage of using a model chemistry such as MP2/6-311+G(2df,2p)//HF/6-31+G(d,p) to compute the enthalpy of a molecule as opposed to just using MP2/6-311+G(2df,2p) alone?

17. There are a plethora of density functionals to choose from, e.g., BLYP, PBE, TPSS, BMK. Why are there so many choices and what are you changing when you change functionals?

18. BMK is an example of a hybrid meta-GGA. What does “hybrid meta-GGA” mean?

19. What is the Polarizable Continuum Method and what is its purpose?

20. Give an example of a situation where an implicit solvation method will fail to give a good answer. Discuss methods to overcome this deficiency of the model.