

1. What do we mean in computational chemistry by a potential energy surface?

2. Identify the points labeled A, B, C, and D in Figure 1 as minima, transition states, or other. Explain your reasoning.

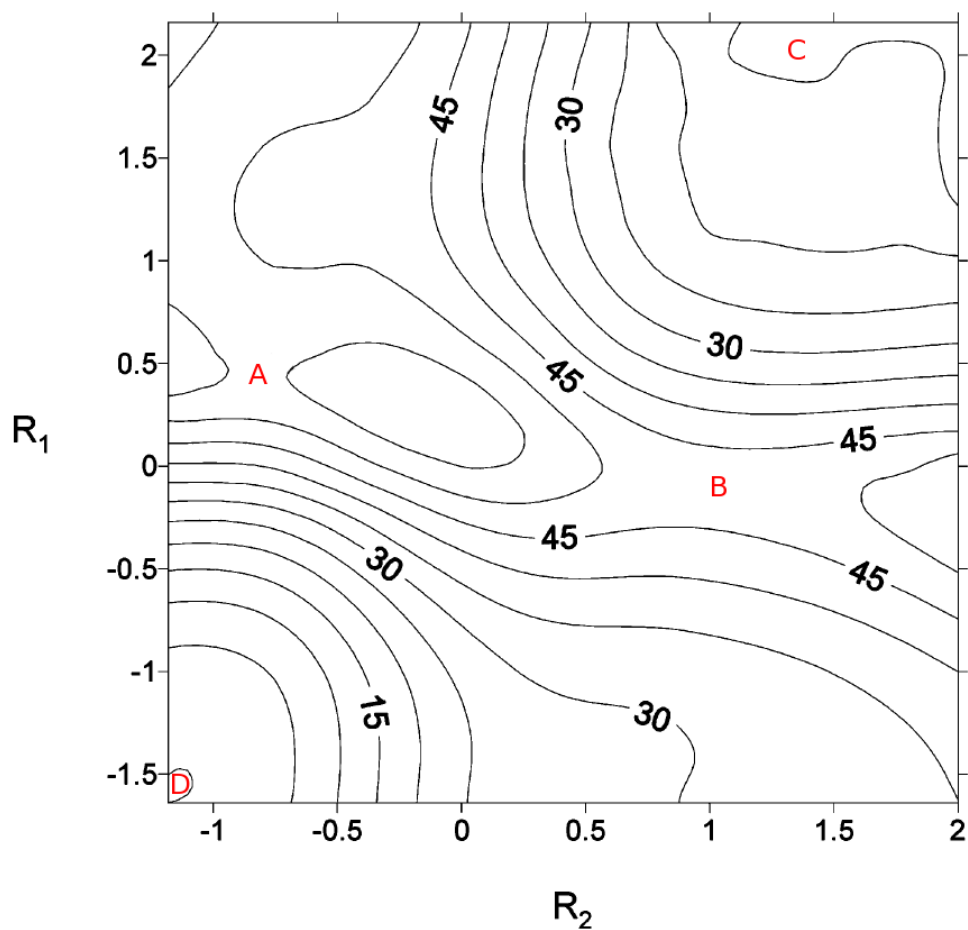


Figure 1: A potential energy surface from Ferrer, et al. *J. Chem. Theory Comput.*, 2005, 1, 750–761.

3. Define one of the minima in Figure 1 as the reactant and another one as the product. For your choice of product and reactant, is the reaction exothermic or endothermic? Explain your reasoning.

4. Identify the points labeled X, Y, and Z in Figure 2 as minima, transition states, or other. Explain your reasoning.

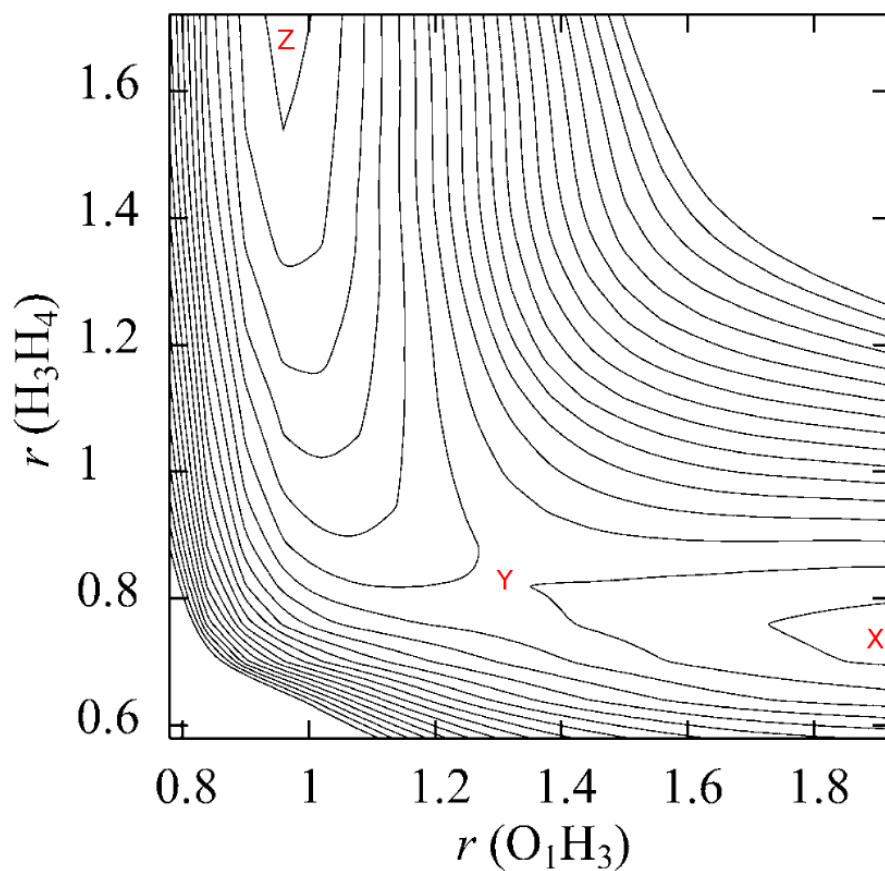


Figure 2: A potential energy surface from Tishchenko, O.; Truhlar, D. G. *J. Chem. Theory Comput.*, **2009**, *5*, 1454–1461.

5. Name 8 properties of a molecule that can be calculated using computational chemistry software.
6. A novice computational chemist is having trouble with a calculation. When he tries to run his calculation, it crashes with the following error: 2000000000 WORDS OF MEMORY UNAVAILABLE. He asks his colleague what this means, and she says, "It means you don't have enough memory to perform your calculation. 2000000000 words is about 16 gigabytes, and your computer probably doesn't have that much memory." The novice computational chemist thanks her and rushes out to the computer store, buys a 250 gigabyte disk drive, installs it in his computer, and tries his calculation again. Alas, he still gets the same error. Why?
7. Suppose a CCSD(T)/6-31G(d,p) calculation containing 500 basis functions took 24 hours to complete.
- (a) If one of the hydrogen atoms in the calculation were replaced by a phenyl group, how many basis functions would be in the resulting calculation?
- (b) CCSD(T) calculations formally scale as $\mathcal{O}(N^7)$. Estimate the time the new calculation with the phenyl group will take to complete.

8. A novice computational chemist realizes that a calculation she want to do will take 1 year to complete using the 2 CPU's in her desktop computer. She see that a computer with 240 CPU's only costs \$125,000 and convinces her department to forgo that fancy mass spectrometer everyone wants so she can buy this "supercomputer" instead. She figures it should only take about three days for her 240 CPU computer to complete that calculation that would have taken her desktop computer (with 2 CPU's) a year to complete. Two months later, her calculation is still running! Why?

9. The energy of a lone electron with principle quantum number n bound to a nucleus with Z protons is given by

$$E_n = -\frac{m_e e^4 Z^2}{32\pi\epsilon_0^2 \hbar^2 n^2}$$

where m_e is the mass of an electron, e is the charge on an electron, and ϵ_0 is the permittivity of vacuum.

What is the energy of a $1s$ electron in an isolated hydrogen atom in *atomic units*?

10. An energy difference is calculated to be 0.18 hartrees. What is that in electron volts?

$$\begin{aligned} 1 \text{ hartree} &= 627.51 \frac{\text{kcal}}{\text{mol}} \\ &= 2.626 \times 10^3 \frac{\text{kJ}}{\text{mol}} \\ &= 27.211 \text{ eV} \\ 1 \text{ bohr} &= 0.529 \text{ \AA} \\ &= 52.9 \text{ pm} \end{aligned}$$

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

12. 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 $\sum_k \sum_l$?

13. In your own words, describe the Born-Oppenheimer approximation and its importance to computational chemistry.

14. If I have computed some approximate ground state wavefunction for a system, let us call it Φ , what does the variational principle tell us about the energy of Φ compared to the actual ground state energy of the system? How do we use this fact in electronic structure calculations?

15. The solution to the equation $\hat{\mathcal{H}}\Psi = E\Psi$ is 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.

16. What is the connection between the Pauli Exclusion Principle and the use of Slater determinants to express electronic wavefunctions?

17. 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?

18. What is the advantage of a split-valence double-zeta basis set over a full double-zeta basis set?

19. How many sets of p functions are on a fluorine atom in the 6-311G(2df,2p) basis set? How many primitive Gaussians are in each of these sets of p functions?
20. What is the degree of contraction of the basis functions for the $1s$ electrons of a fluorine atom in the 6-31G(d) basis set?
21. What is the difference between the 6-31G(d,p) basis set and the 6-31+G(d,p) basis set?
22. Which basis set is more balanced in its polarization, 6-31G(3df) or 6-311G(2df)? Explain your answer.
23. What is the advantage of using an ECP-basis set combination like LanL2DZ for calculations involving atoms like cadmium?

24. If a molecule has two unpaired electrons, like O_2 , what is the value of the multiplicity we should specify when trying to do an electronic structure calculation of the ground state of such a system. Explain how you computed your answer.
25. Why is it a good idea to calculate the Hessian matrix at a stationary point even if you don't care about the vibrational frequencies?