Computational chemistry I assignments Quantum part Feb. 2024

Essay: Answer to these questions.

1) Explain the k-points. Why do you need to test them. If you increase the simulation cell what you can do for k-points. Explain the band structure. What do the band structure lines really mean? What is the Fermi energy? Which bands are occupied which are empty.

2) Explain the surface symmetry classifications of both clean and adsorbate containing surfaces. What is the surface unit cell. Find some examples of reconstructions and molecules adsorbing on the surface. How will they change the symmetry?

Below are some symmetries of water absorbance on some metal surfaces. (from Henderson, Surf. Sci. Rep. 46, p. 1-308 (2002). Explain what the symmetries are.

surface	symmetry	temp
Ni(1 1 0)	c(2×2)	180
Ni(1 1 0)	c(2×2)	80–150
Ni(1 1 1)	(√3×√3)R30°	80
	(√3×√3)R30°	120
Pd(1 1 0)	c(2×2)	100
	c(2×2)	100
Pt(1 1 1)	(√3×√3)R30°	100
	(√37×√37)R25.3° and (√39×√39)R16.1° domains[a]	130

3) Explain how reaction barriers can be computed. (with general terms, no math details are needed). Why the barrier calculations are slow? What are the BEP (Brønsted–Evans–Polanyi) relation and volcano plot? Why they are useful for predicting chemical reaction rates. Give some examples of both of them. A good but a bit technical article of the volcano plot can be found form: http://www.beilstein-journals.org/bjnano/single/articleFullText.htm?publicId=2190-4286-5-96

Computational assignments (choose 2)

C1) Investigate P-P, Ge-Ge and vacancy-P interaction in Si. Use 64 atom unit cell. Do one calculation with the impurity atoms (or vacancy) next to each other and another further away. Relax the system. Interpret the results. Will the atoms prefer to be next to each other or the vacancy or further away? Pay attention to the size of the energy difference. Give the total and relative energies. (In GPAW all energies are in eV's, 1 eV = 96.48 kJ/mol, room temp RT = 2.44 kJ/mol)

C2) Investigate Ag enrichment on Cu(111) surface. Do a slab calculation with (1x1) surface and 1 Ag atom in the slab. How thick slab do you need to choose? Where the Ag prefers to be. Repeat the calculation with (2x2) surface and with 1 Ag atom. Relax the system. On the (2x2) system add one O atom to the surface hollow site and repeat the Ag position calculations. In this case, you can use a 4-atom Ag layer or a single atom. In the single atom case, there are more O-Ag combinations on the surface, so explain how you do the calculations. Does O change the Ag enrichment?

C3) Compare CO adsorption energies to Pt(111), Ag(111), Rh(111) surfaces. Use the (2x2) surface. In which site (ontop, bridge or fcc) the CO prefer to be. Which surface has the strongest binding energy? Use h=0.18 and 2x2x1 k-points.

C4) Do a NEB calculation of CO dissociation on Pt(111) 2x3 surface. You need the CO and atomic C and O adsorption as input. The C and O atoms have to be on fcc sites on the long unit cell side. Use 16 or 24 cores (jsub -np 16 -mem 2G gpaw …). Explain the reaction path. Are the Pt atoms static? What are the barrier and reaction energy? The convergence is not easy in any NEB computation. Check the *NEB*.log file. If it has taken more than a day and the force is below ca. 0.3 it can be ended (the convergence criteria is 0.2, see also the total energy in the *NEB*log file).

You should do **the E assignments** and **2 C assignments** from the total list above. You will get 20 p. form the essay assignments and 10 p. form the computational ones. (Total 40 p)

The E assignment report should be around 8 pages (2-3 pages per question) and each C assignment around 3 pages. You can include pictures in the reports. All material you find can be used but do not copy directly any source, like Wikipedia or similar. The use of AI-based tools (Chat-GPT, etc) for the assignment is NOT allowed. Please use some references in the Essay. When presenting the computational results, you should use tables and/or pictures. The pictures can be taken from the screen. When returning the assignments, put your NAME, STUDENT NUMBER and the number of assignment (like E or C2) to the filename.