

Evaluation of the Quantum Essays in Comp Chem I

Corrections notes: Not everything of these need to be in the essay. NOTE these are not answer examples only topics that should be in the essay.

E1: Explain the k-points. What they mean. If you increase the simulation cell what you can do for k-points. Explain the band structure. What the band structure lines really mean?

k-points. In periodic potential $U(\mathbf{r}+\mathbf{R})=U(\mathbf{r})$, where \mathbf{R} is the periodicity vector, $\mathbf{R}=n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, where \mathbf{a} 's are the cell vectors. We can define reciprocal vectors, \mathbf{k} , for $\mathbf{R}\cdot\mathbf{k}=2\pi N$ and $\mathbf{k}=\mathbf{m}_1\mathbf{b}_1+\mathbf{m}_2\mathbf{b}_2+\mathbf{m}_3\mathbf{b}_3$ where \mathbf{b} 's are reciprocal cell vectors. (they depend on the cell symmetry, $\mathbf{b}_1=\mathbf{a}_2\times\mathbf{a}_3/\text{vol}(\text{unit cell})$ etc). The smallest independent \mathbf{k} -values form a Brillouin zone (BZ). Its shape depend on the symmetry. A picture of FCC BZ would be good. If you increase the computational cell (or the \mathbf{a} 's) you will need less \mathbf{k} -points. If you double the cell in x-dir you need $\frac{1}{2}$ the \mathbf{k} -points in x-dir.

The Bloch theorem states that the wavefunction is $\exp(-i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{n},\mathbf{k}}(\mathbf{r})$ where $u(\mathbf{r})$ is on the unit cell and $\exp(-i\mathbf{k}\cdot\mathbf{r})$ is a phase factor or it describes the symmetry of the wf. At Γ -point $\mathbf{k}=(0,0,0)$ the wf have the same symmetry as the unit cell. At X point $\mathbf{k}=(1/2,0,0)$ the wf has symmetry of two unit cells in x-direction and unit cell symm in y- and z-directions.

The system has usually high symmetry. In cubic system $\text{wf}(\mathbf{k}=(k_x,0,0))=\text{wf}(\mathbf{k}=(0,k_x,0))=\text{wf}(\mathbf{k}=(0,0,k_x))$ and many more.

We need to solve the wf's (and eigenvalues $\epsilon_{\mathbf{n},\mathbf{k}}$) at several \mathbf{k} -points, like $8\times 8\times 8$ grid. The Monkhorst-Pack scheme is very common. Eigenvalues $H\Psi_{\mathbf{n},\mathbf{k}} = \epsilon_{\mathbf{n},\mathbf{k}}\Psi_{\mathbf{n},\mathbf{k}}$

Density (and total energy) need a sum over the \mathbf{k} -points $\rho(\mathbf{r}) = \sum_{\mathbf{n},\mathbf{k}} |u_{\mathbf{n},\mathbf{k}}(\mathbf{r})|^2$

Band structure: the band structure describes the energy eigenvalues of the Schrödinger (or DFT) equation at given \mathbf{k} -point. Typically, the lowest value is at Γ -point. A picture of Si band structure would be good. In isolated molecule only discrete eigenvalues are obtained. In periodic systems the eigenvalues form energy bands. Inside of the band all energies are possible.

There can be gaps between the bands. Example: "HOMO-LUMO" band gap. but there can be others. See the NaCl band structure.

E2: Explain the surface symmetry classifications of both clean and adsorbate containing surfaces. Find some examples of reconstructions and molecules adsorbing on the surface. How they will change the symmetry?

Surface depend on the crystal structure and in any material, we can cut the system (to form a surface) in many ways. The cut direction is usually described with the Miller index. E.g. FCC(111) surface. On any perfect surface there is a periodic 2D ordered unit cell. This is the (1x1) surface. A picture of FCC(111) would be good.

There are several ways the symmetry can be broken. If a CO molecule will adsorb on Pt(111) surface it cannot fill every (1x1) units cell because there is strong short range repulsion on CO@Pt(111). Let us look the CO at coverage of $\frac{1}{4}$ (one CO per 4 Pt). This very likely form a symmetric (2x2) surface unit cell (4 atoms or 4 (1x1) unit cells). With more complicated molecules, like water, the surface cell can be much larger. See examples in the lecture notes.

The general notation of surface unit cell is $(n\times m)R\theta$ where θ is the rotation angle of the surface cell with respect to the original cell. here a picture would be good

You can also discuss the adsorbent sites, top, hollow and Bridge.

The reconstructions will also lower the symmetry and the surface unit cell of a reconstructed surface is larger. like (2c2). The reference is always an ideal surface. Pictures and examples are useful.

E3: Explain what are the BEP (Brønsted–Evans–Polanyi) relation and the 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>.

BEP relates the reaction barrier E_b to reaction energy ΔE $E_b = \alpha \Delta E + \beta$ here α are β fitting parameters ($\alpha > 0$). The BEP relation need to be tested. Sometimes it works sometimes not. pictures and examples are needed. Why to use BEP? The barrier calculation is at least 10x slower than the energy calc. We can test much more potential reaction is BEP works.

Volcano plot is a visualization of the Sabatier principle. The idea is that if binding to the catalyst (often a surface) is too weak it is not a good catalyst. It does not influence the chem bonding. The other extreme is when the molecules (or one molecule) bind to the surface very strongly. This can cause catalyst poisoning (the strongly bound molecule will fill the whole surface) or the surface diffusion can be very slow. The height of the volcano (usually logarithm scale) is the reaction rate (either exp measured of the comp barrier). The x-axis is usually some binding energy (often computed). The trick is to find a good binding energy. With the Volcano plot the good catalyst search will focus close to the optimal binding energies. Some examples and pictures are needed.