Questions for lecture 11 (non-adiabatic dynamics)

1. Derive Time-dependent Schrödinger equation (TDSE) on slide 8 for a vibrational wavepacket (refresh your 101 quantum mechanics!)

$$i\hbar\frac{\partial\chi_a(\boldsymbol{R},t)}{\partial t}=\Big[-\frac{1}{2}\hbar^2\nabla_{\boldsymbol{R}}\cdot\widehat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\nabla_{\boldsymbol{R}}+E_a(\boldsymbol{R})-\sum_b\frac{1}{2}\hbar^2\,\boldsymbol{d}_{ab}(\boldsymbol{R})\cdot\widehat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\boldsymbol{d}_{ab}(\boldsymbol{R})\Big]\chi_a(\boldsymbol{R},t)$$
$$+\sum_b\frac{1}{2}\hbar^2\big[\boldsymbol{d}_{ab}(\boldsymbol{R})\cdot\widehat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\nabla_{\boldsymbol{R}}+\nabla_{\boldsymbol{R}}\cdot\widehat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\boldsymbol{d}_{ab}(\boldsymbol{R})\big]\chi_b(\boldsymbol{R},t)$$

From a general TDSE $i\hbar\dfrac{\partial\Psi(\boldsymbol{R},\boldsymbol{r},t)}{\partial t}=\widehat{H}(\boldsymbol{R},\boldsymbol{r})\Psi(\boldsymbol{R},\boldsymbol{r},t)$

Hint: use kinetic energy in $\widehat{H}(\boldsymbol{R},\boldsymbol{r})=\widehat{T}(\boldsymbol{R})+\widehat{H}_{el}(\boldsymbol{R},\boldsymbol{r})$

As $\widehat{T}(\boldsymbol{R})=-\frac{1}{2}\hbar^2\nabla_{\boldsymbol{R}}\cdot\widehat{\boldsymbol{m}}_{\boldsymbol{R}}^{-1}\cdot\nabla_{\boldsymbol{R}}$ and utilize other expressions on the slide

2. Phonon bottleneck appears when there are energetic gaps between bands in electronic spectra of molecules or solids. In few sentences, discuss its importance for non-radiative relaxation and technologically important phenomena such as hot electron extraction, multiexciton generation, etc.

3. In few sentences, describe examples of non-adiabatic dynamics in your research (e.g. non-radiative relaxation, internal conversion, intersystem crossing, etc.). Why is this important (or not important) for processes you are studying?