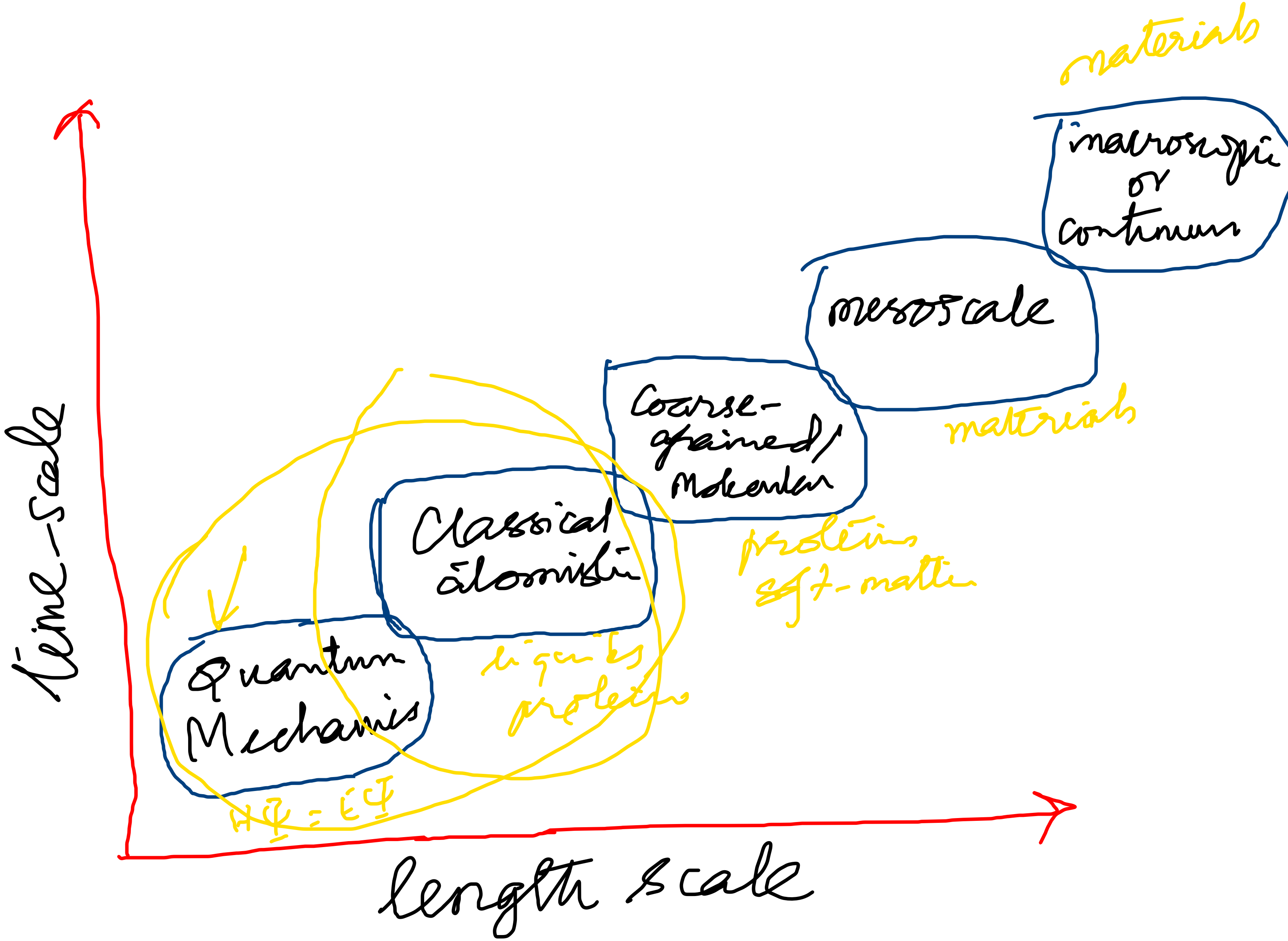
time-scale
length scale
Quantum Mechanics
$H\Psi = E\Psi$
Classical atomistic
liquids
proteins
Coarse-grained/ Molecular
proteins
soft-matter
mesoscale
materials
macroscopic or continuum
materials

Lecture 2: Potential Energy Surfaces

electron nuclei

$$i\hbar \frac{\partial}{\partial t} \Phi(\{\vec{r}_i\},\{\vec{R}_I\},t) = \hat{H}\, \Phi(\{\vec{r}_i\},\{\vec{R}_I\},t) \qquad (1)$$

$\Phi \rightarrow$ T.D. wavefunction of the entire system of N atoms & their electrons.

$$\hat{H} = \sum_I \frac{\hat{P}_I^2}{2M_I} + \sum_i \frac{\hat{p}_i^2}{2m_e} + \frac{1}{4\pi\epsilon_0}\sum_{i<j} \frac{e^2}{r_{ij}} - \frac{1}{4\pi\epsilon_0}\sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} + \sum_{I<J} \frac{Z_I Z_J}{4\pi\epsilon_0 R_{IJ}} \qquad (2)$$

$|\vec{r}_i - \vec{r}_j|$

$$\hat{H} = \sum_{I} \frac{\hat{P}_I^2}{2M_I} + \hat{H}_{el}\left(\{\vec{r}_i\};\{\vec{R}_I\}\right) + \frac{1}{4\pi\epsilon_0}\sum_{I<J}\frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad \text{--- (3)}$$

$$\hat{H}_{el}\left(\underbrace{\{\vec{r}_i\}}_{\vec{r}};\underbrace{\{\vec{R}_I\}}_{\vec{R}}\right) = \sum_{i} \frac{\hat{p}_i^2}{2m_e} + \frac{1}{4\pi\epsilon_0}\sum_{i<j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \frac{1}{4\pi\epsilon_0}\sum_{i,I}\frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} \quad \text{--- (4)}$$

$$\hat{H}_{el}(\vec{r};\vec{R})\,\Psi_n(\vec{r};\vec{R}) = E_n(\vec{R})\,\Psi_n(\vec{r};\vec{R}) \quad \text{--- (5)}$$

Clamped nuclear Schrödinger eqn.

$$\Phi(\vec{r},\vec{R},t) = \sum_n \underline{\chi_n(\vec{R},t)\,\Phi_n(\vec{r};\vec{R})} \quad — (6)$$

expansion in adiabatic basis & also Born-Huang representation. ($\{\Phi_n\}$ form a complete set)

Substitute (6) in (1) :

$$i\hbar \sum_n \frac{\partial \chi_n(\vec{R},t)}{\partial t}\,\Phi_n(\vec{r};\vec{R})$$

$$= \sum_n \sum_I \frac{\hat{P}_I^2}{2M_I}\left(\chi_n(\vec{R},t)\,\Phi_n(\vec{r};\vec{R})\right) \quad — (7)$$

$$+ \sum_n \chi_n(R,t)\,\hat{U}(R_I)\,\Phi_n(\vec{r};\vec{R})$$

$$\hat{U}(\vec{R}) = \hat{H}_{el}(\vec{R}) + \frac{1}{4\pi\epsilon_0}\sum_{I<J}\frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} \quad \text{— (8)}$$

Given that $\hat{p}_I = \frac{\hbar}{i}\vec{\nabla}_I$ (in position representation)

$$\frac{\hat{p}_I^2}{2M_I}\left(\chi_n(\vec{R})\,\Psi_n(\vec{r};\vec{R})\right) = -\frac{\hbar^2}{2M_I}\vec{\nabla}_I\cdot\vec{\nabla}_I\left(\chi_n\Psi_n\right)$$

$$= -\frac{\hbar^2}{2M_I}\Big[\underline{(\nabla_I^2\Psi_n)}\chi_n + \underline{2(\nabla_I\Psi_n)\cdot\nabla_I\chi_n}$$

$$+ \underline{\underline{\Psi_n\nabla_I^2\chi_n}}\Big] \quad \text{— (9)}$$

Multiply (7) by $\Phi_m^*(\vec{r};\vec{R})$ from the left and integrate over all $\vec{r} \equiv (\vec{r}_1, \vec{r}_2, \dots)$

$$i\hbar \frac{\partial}{\partial t} \chi_m(\vec{R},t) = \sum_n \left\{ \hat{C}_{mn} + \hat{D}_{mn} \right\} \chi_n(\vec{R},t) \quad \text{— I}$$

$$+ \left\{ \sum_I \frac{\hat{P}_I^2}{2M_I} + U_m(\vec{R}) \right\} \chi_m(\vec{R},t) \quad \text{— II}$$

— (10)

$$U_m(\vec{R}) = E_m(\vec{R}) + \frac{1}{4\pi\epsilon_0} \sum_{I<J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 R_{IJ}}$$

— (11)

$$\hat{C}_{mn}(\vec{R}) = \sum_I \left\langle \Phi_m \left| \frac{\hat{P}_I^2}{2M_I} \right| \Phi_n \right\rangle_e \Rightarrow \int d^3r_1 \int d^3r_2 \cdots \quad — (12)$$

$$\hat{D}_{mn}(\vec{R}) = \sum_I \left\langle \Phi_m \left| \frac{-\hbar^2}{M_I} \vec{\nabla}_I \right| \Phi_n \right\rangle \cdot \vec{\nabla}_I \quad — (13)$$

If C & D were zero then there is no mixing between electronic eigenstates during dynamics. If not then the system evolves by causing transition among $\{\Phi_n\}$

$C \,\&\, D = 0 \Rightarrow$ Adiabatic dynamics and constitute the adiabatic approximation

Actually for eqns to be decoupled we only need that C_{mn} & D_{mn} go to zero for $m \neq n$. In the case the eqn for χ_m becomes:

$$i\hbar \frac{\partial \chi_m(\vec{R},t)}{\partial t} = \left\{ \sum_I \frac{\hat{P}_I^2}{2M_I} + \overbrace{\hat{U}_m(\vec{R}) + C_{mm}(\vec{R}) + D_{mm}(\vec{R})}^{\tilde{U}_m(\vec{R})} \right\} \chi_m(\vec{R},t) \quad (14)$$

To be precise this is the adiabatic approx.

If C_{mm} & D_{mm} are also taken to be zero then we get the Born-Oppenheimer approx.

$$i\hbar \frac{\partial \chi_m(\vec{R},t)}{\partial t} = \underbrace{\left\{ \sum_I \frac{\hat{P}_I^2}{2M_I} + U_m(\vec{R}) \right\}}_{\hat{H}_N} \chi_m(\vec{R},t) \quad \text{— (15)}$$

$\hat{P}_I \nearrow T$ $U_m(\vec{R}) \nearrow$ P. E.

$U_m(\vec{R}) \longrightarrow$ Potential energy surface of the m^{th} electronic eigenstate

$$\vec{R} \equiv \{ \vec{R}_1, \vec{R}_2, \ldots \vec{R}_N \}$$