

The Car-Parrinello equations of motion

We plug the Car-Parrinello Lagrangian:

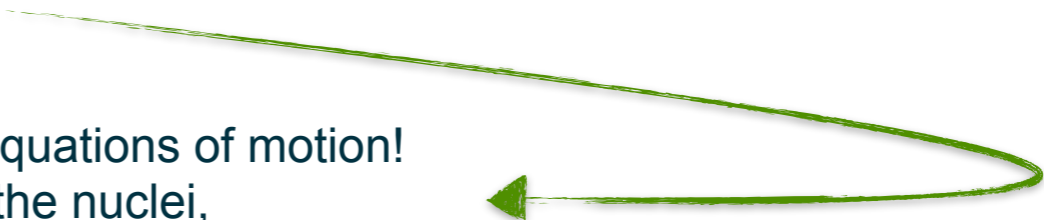
$$\mathcal{L}_{CP}(\mathbf{R}_{nu}, \phi_{el}, \dot{\mathbf{R}}_{nu}, \dot{\phi}_{el}) = \frac{1}{2} \sum_{i=1}^{N_{nu}} m_{nu,i} \dot{\mathbf{R}}_{nu,i}^2 + \frac{1}{2} \mu \sum_{j=1}^{N_{el}} \langle \dot{\phi}_{el,j} | \dot{\phi}_{el,j} \rangle - E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\}) + \sum_{j,k} \Lambda_{j,k} (\langle \phi_{el,j} | \phi_{el,k} \rangle - \delta_{j,k})$$

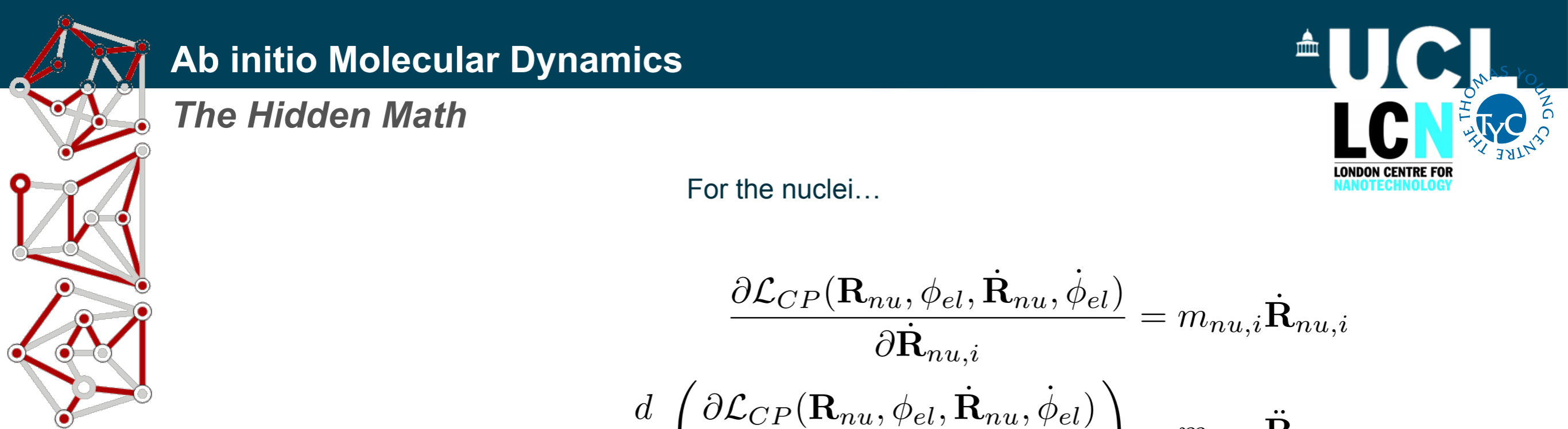
Into the Eulero-Lagrange equation:

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} \right) - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = 0$$

The CP Lagrangian is a function of both the ionic AND the electronic degrees of freedom...

Two **COUPLED** equations of motion!
One for the nuclei,
one for the electrons





Ab initio Molecular Dynamics

The Hidden Math

For the nuclei...

$$\frac{\partial \mathcal{L}_{CP}(\mathbf{R}_{nu}, \phi_{el}, \dot{\mathbf{R}}_{nu}, \dot{\phi}_{el})}{\partial \dot{\mathbf{R}}_{nu,i}} = m_{nu,i} \dot{\mathbf{R}}_{nu,i}$$

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}_{CP}(\mathbf{R}_{nu}, \phi_{el}, \dot{\mathbf{R}}_{nu}, \dot{\phi}_{el})}{\partial \dot{\mathbf{R}}_{nu,i}} \right) = m_{nu,i} \ddot{\mathbf{R}}_{nu,i}$$

$$\frac{\partial \mathcal{L}_{CP}(\mathbf{R}_{nu}, \phi_{el}, \dot{\mathbf{R}}_{nu}, \dot{\phi}_{el})}{\partial \mathbf{R}_{nu,i}} = - \left. \frac{\partial}{\partial \mathbf{R}_{nu,i}} \right|_{\langle \phi_{el,j} | \phi_{el,k} \rangle = \delta_{j,k}} [E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\})]$$

$$= - \frac{\partial E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\})}{\partial \mathbf{R}_{nu,i}} + \sum_{j,k} \Lambda_{j,k} \frac{\partial}{\partial \mathbf{R}_{nu,i}} \langle \phi_{el,j} | \phi_{el,k} \rangle$$

$$\rightarrow m_{nu,i} \ddot{\mathbf{R}}_{nu,i} = - \frac{\partial E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\})}{\partial \mathbf{R}_{nu,i}} + \sum_{j,k} \Lambda_{j,k} \frac{\partial}{\partial \mathbf{R}_{nu,i}} \langle \phi_{el,j} | \phi_{el,k} \rangle$$

$$\frac{\partial \mathcal{L}_{CP}(\mathbf{R}_{nu}, \phi_{el}, \dot{\mathbf{R}}_{nu}, \dot{\phi}_{el})}{\partial \langle \dot{\phi}_{el,j} |} = \mu \dot{\phi}_{el,j} \quad \text{as} \quad \langle \dot{\phi}_{el,j} | \dot{\phi}_{el,j} \rangle = ||\dot{\phi}_{el,j}||^2$$

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}_{CP}(\mathbf{R}_{nu}, \phi_{el}, \dot{\mathbf{R}}_{nu}, \dot{\phi}_{el})}{\partial \langle \dot{\phi}_{el,j} |} \right) = \mu \ddot{\phi}_{el,j}$$

$$\frac{\partial \mathcal{L}_{CP}(\mathbf{R}_{nu}, \phi_{el}, \dot{\mathbf{R}}_{nu}, \dot{\phi}_{el})}{\partial \langle \phi_{el,j} |} = - \left(\frac{\partial}{\partial \langle \phi_{el,j} |} \Big|_{\langle \phi_{el,j} | \phi_{el,k} \rangle = \delta_{j,k}} [E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\})] \right) + \sum_k \Lambda_{j,k} |\phi_{el,k} \rangle$$

$$\rightarrow \mu \ddot{\phi}_{el,j} = - \left(\frac{\partial}{\partial \langle \phi_{el,j} |} \Big|_{\langle \phi_{el,j} | \phi_{el,k} \rangle = \delta_{j,k}} [E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\})] \right) + \sum_k \Lambda_{j,k} |\phi_{el,k} \rangle$$