The Car-Parrinello equations of motion

We plug the Car-Parrinello Lagrangian:

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

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

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

The Hidden Math

For the nuclei…

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

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

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

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

and for the electrons…

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

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

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

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