Machine Learned Orbital Free DFT: Taking the Next Step

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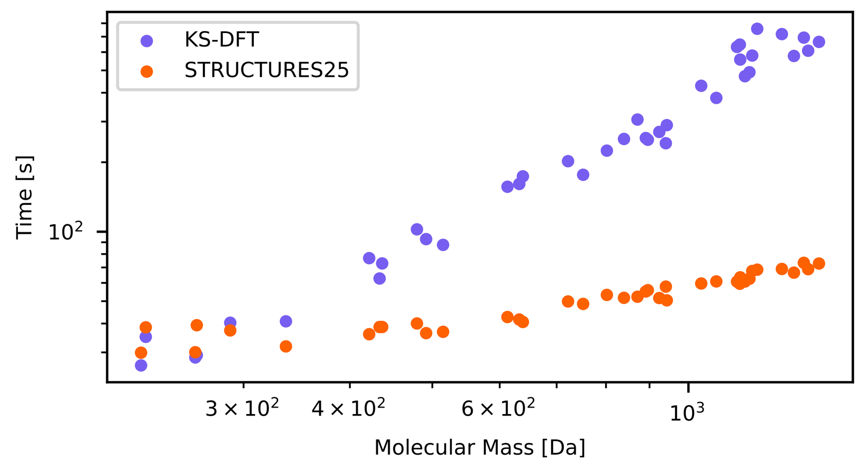
The Vision of ML-OF-DFT

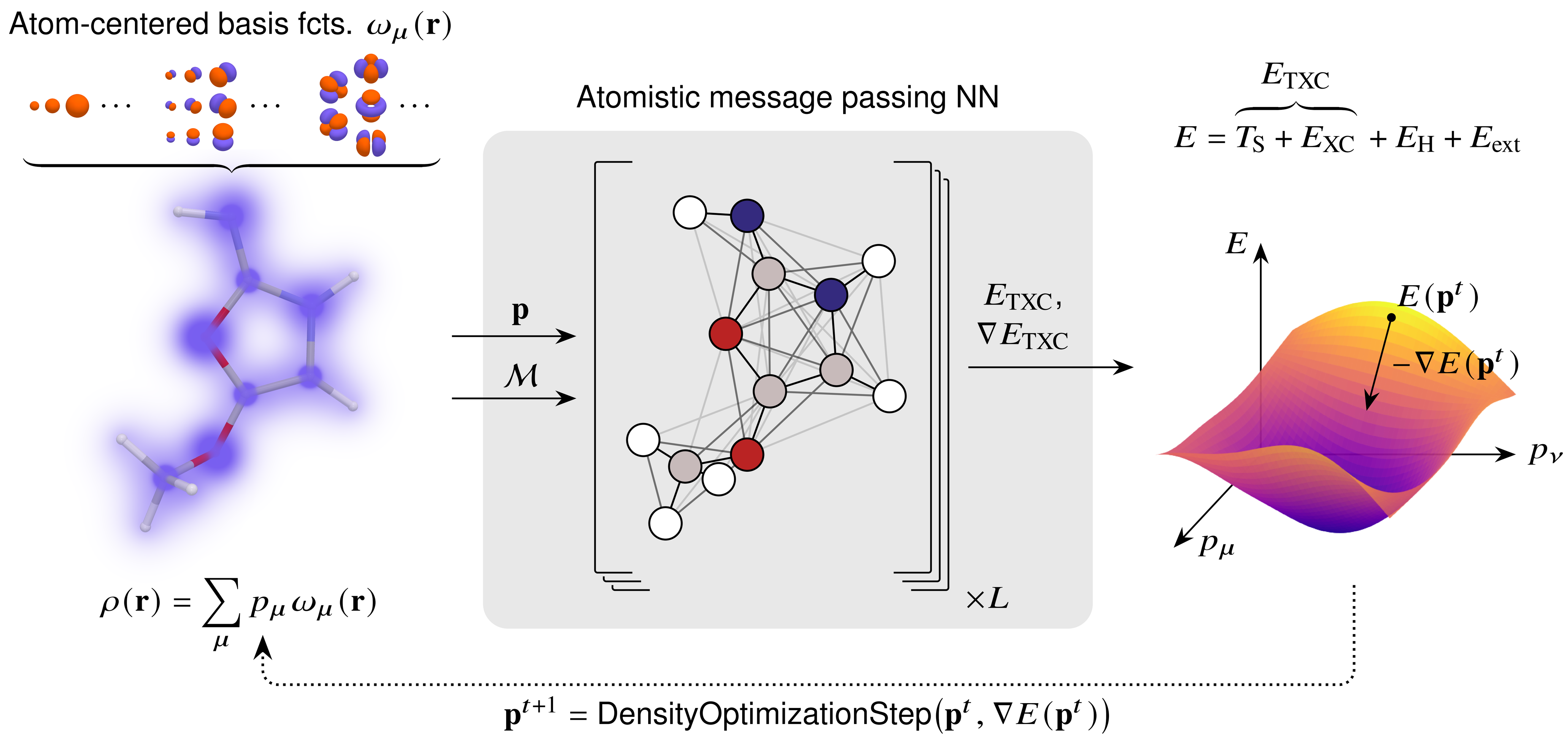
- Orbital Free Density Functional Theory (OF-DFT) promises nearly linear scaling



- Retaining as much of physics as possible
- Natural inclusion of environment effects
- Enabling quantum mechanical simulations rather than circumventing them like ML interatomic potentials

KS-DFT Accuracy at OF-DFT Speed

ML-OF-DFT Workflow



Analytical Nuclear Gradients

Model/Architecture dependent basis transformation

Pulay-like Terms — basis function dependence

Hellmann-Feynman-Terms — explicit dependence on R_A

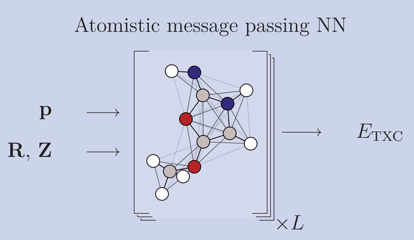
Stationary point, constant N_e $= 0$

$$\frac{\mathrm{d}E^{\mathrm{ML}}_{\mathrm{TXC}}(\mathbf{p}_0,\mathbf{R})}{\mathrm{d}R_A}\bigg|_{\mathbf{p}_0} = \underbrace{\frac{\partial E^{\mathrm{ML}}_{\mathrm{TXC}}(\mathbf{p},\mathbf{R})}{\partial R_A}\bigg|_{\mathbf{p}_0} + \frac{\partial E^{\mathrm{ML}}_{\mathrm{TXC}}(\tilde{\mathbf{p}},\mathbf{R})}{\partial \tilde{\mathbf{p}}}\bigg|_{\mathbf{R}} \frac{\partial \mathbf{X}}{\partial R_A}\mathbf{p}_0}$$

$$\frac{\mathrm{d}E_{\mathrm{tot}}(\mathbf{p}_0,\mathbf{R})}{\mathrm{d}R_A} = \frac{\mathrm{d}E^{\mathrm{ML}}_{\mathrm{TXC}}(\mathbf{p}_0,\mathbf{R})}{\mathrm{d}R_A}\bigg|_{\mathbf{p}_0} + \mathbf{p}_0^T \frac{\partial \mathbf{J}}{\partial R_A}\mathbf{p}_0 + \underbrace{\mathbf{p}_0^T \frac{\partial \mathbf{v}_{\mathrm{ext}}}{\partial \omega}\frac{\partial \omega}{\partial R_A} + \mathbf{p}_0^T \frac{\partial \mathbf{v}_{\mathrm{ext}}}{\partial v_{\mathrm{ext}}}\frac{\partial v_{\mathrm{ext}}}{\partial R_A}} + \frac{\partial V_{\mathrm{nn}}(\mathbf{R})}{\partial R_A} + \overbrace{\frac{\partial E_{\mathrm{tot}}(\mathbf{p}_0,\mathbf{R})}{\partial \mathbf{p}}}^{=0}\frac{\partial \mathbf{p}}{\partial R_A}$$

$$E_{\mathrm{tot}}(\mathbf{p};\mathbf{R}) = E^{\mathrm{ML}}_{\mathrm{TXC}}(\mathbf{p};\mathbf{R}) + \tfrac{1}{2}\mathbf{p}^T\mathbf{J}\mathbf{p} + \mathbf{p}^T\mathbf{v}_{\mathrm{ext}} + V_{\mathrm{nn}}$$

Read More About Our Alternative Ansatz: Surrogate Functionals



$$\mathbf{J}_{\mu\nu} = \int \frac{\omega_\mu(r)\omega_\nu(r')}{|r-r'|}$$

$$\mathbf{v}_{\mathrm{ext}} = \int \omega_\mu(r)\, v_{\mathrm{ext}}(r)$$

$$V_{\mathrm{nn}} = \sum_{A \neq B} \frac{Z_A Z_B}{|R_A - R_B|}$$

Kinetic + XC | **Coulomb** | **Environment + Nuc. Attraction** | **Nuc. Repulsion**

Read More About How We Achieve: $\frac{\partial E_{\mathrm{tot}}}{\partial \mathbf{p}} = \mathbf{0}$

STRUCTURES25

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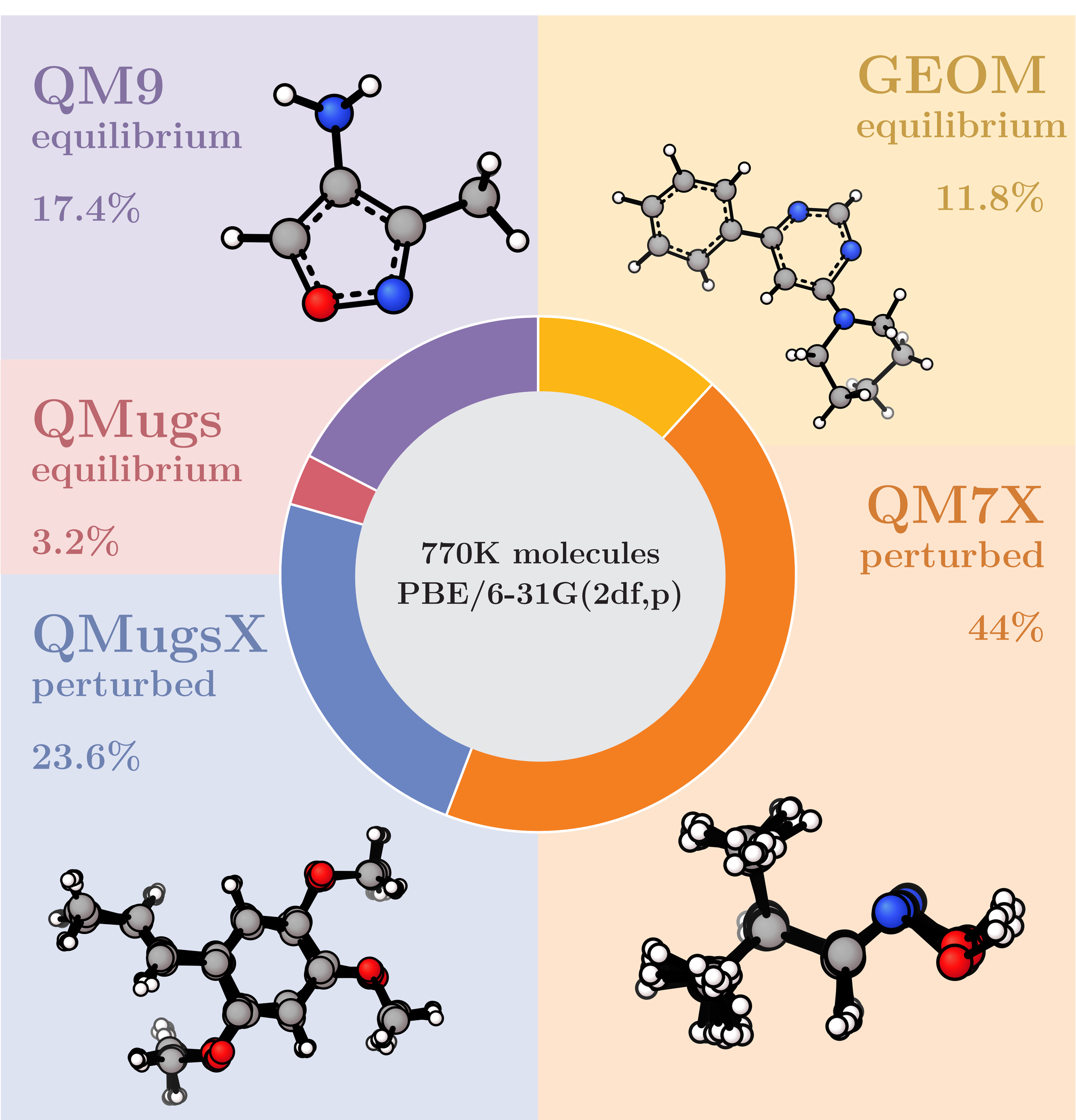
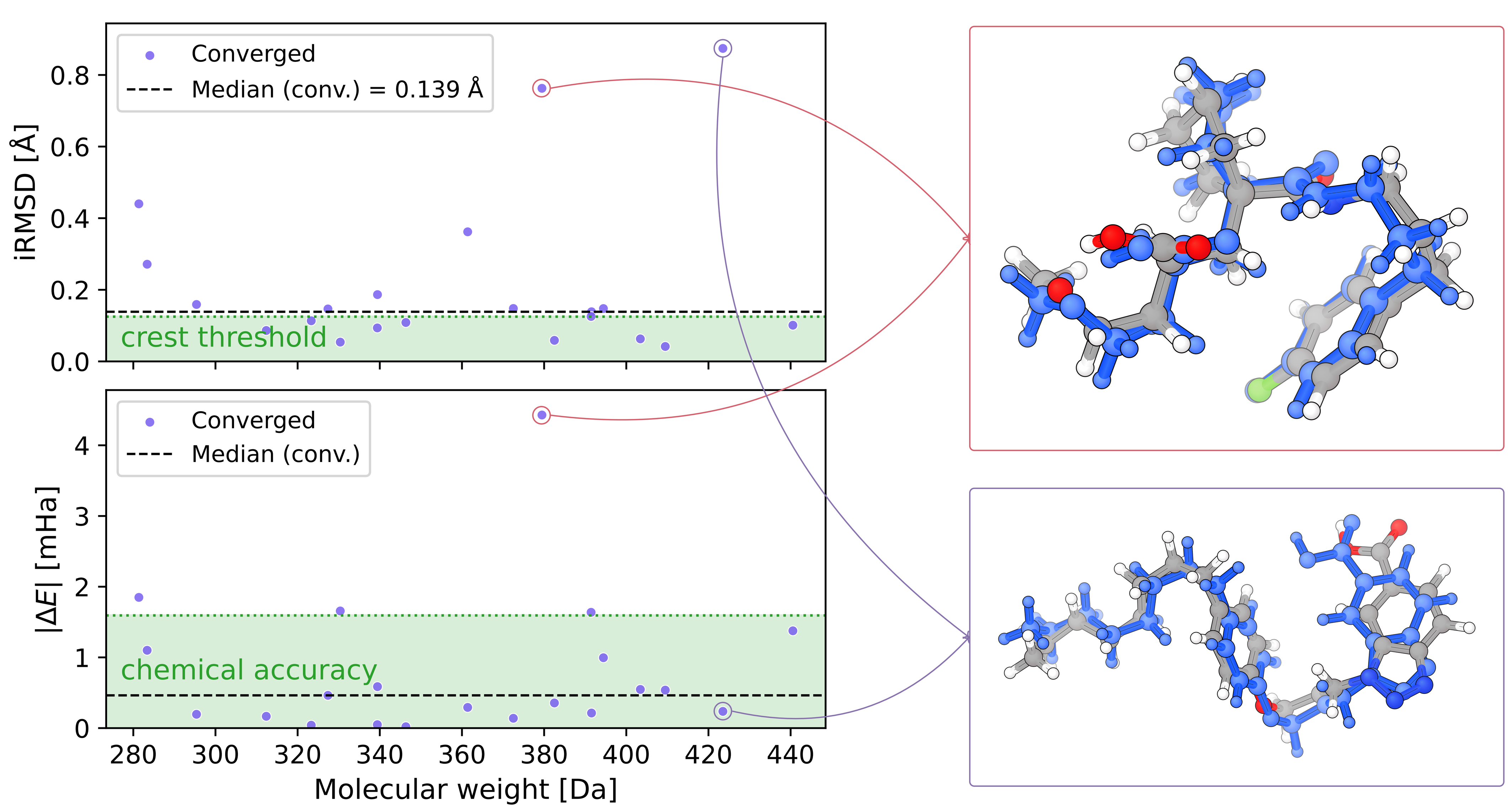
Training Data



Application: Geometry Optimization



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Acknowledgements

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