Electronic structure properties from an atom-centered predictions of the electron density
Supporting Information

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I. ELECTRONIC ENERGY DECOMPOSITION OF LIQUID WATER

The electronic energy of the system can be decomposed in kinetic, electrostatic and exchange-correlation terms. We report below learning curves for each of these terms.
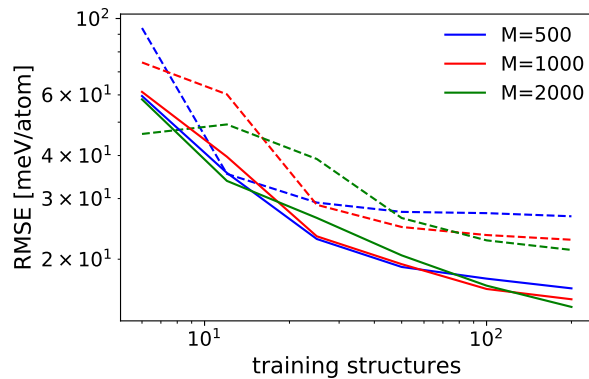

FIG. S1. Learning curves associated with the prediction of 500 randomly selected liquid water structures using models constructed with an increasing number of sparse environments M. absolute RMSE in meV/atom of the kinetic energies obtained by feeding the predicted electron densities into the density functional used to generate the reference data. Full and dashed lines correspond to non-orthogonal and orthogonal learning models, respectively.
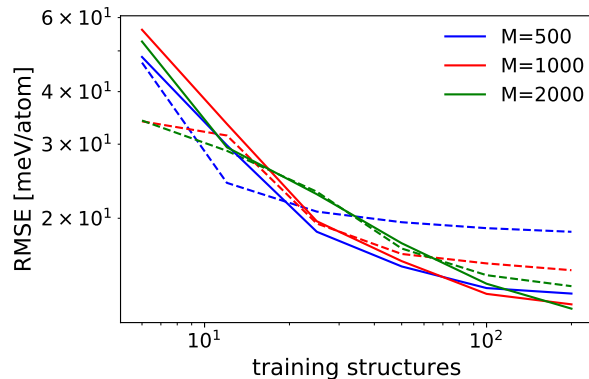

FIG. S2. Learning curves associated with the prediction of 500 randomly selected liquid water structures using models constructed with an increasing number of sparse environments M. absolute RMSE in meV/atom of the electrostatic energies obtained by feeding the predicted electron densities into the density functional used to generate the reference data. Full and dashed lines correspond to non-orthogonal and orthogonal learning models, respectively.
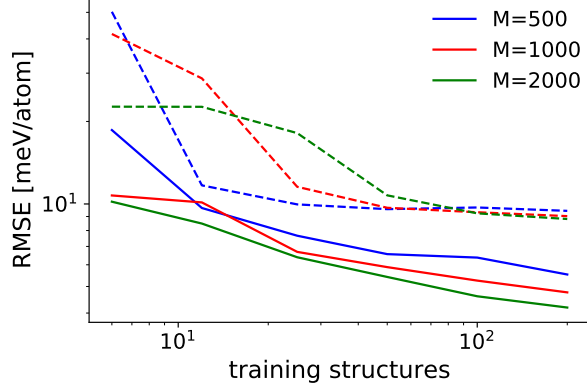
FIG. S3. Learning curves associated with the prediction of 500 randomly selected liquid water structures using models constructed with an increasing number of sparse environments M. absolute RMSE in meV/atom of the exchange-correlation energies obtained by feeding the predicted electron densities into the density functional used to generate the reference data. Full and dashed lines correspond to non-orthogonal and orthogonal learning models, respectively.

II. QUADRATIC APPROXIMATION OF THE TOTAL ENERGY ERROR

Let us consider the decomposition of the predicted density in a reference and error term as $\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \Delta\rho(\mathbf{r})$. For small errors $\Delta\rho$, we can approximate the total energy E through a second-order functional expansion about ρ_0:

$$E[\rho] \approx E[\rho_0] + \int d\mathbf{r} \left(\frac{\delta E}{\delta\rho(\mathbf{r})} \right)_{\rho=\rho_0} \Delta\rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \left(\frac{\delta^2 E}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right)_{\rho=\rho_0} \Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}') \quad \text{(S1)}$$

Given that $\left(\frac{\delta E}{\delta\rho(\mathbf{r})} \right)_{\rho=\rho_0} = 0 \quad \forall\, \mathbf{r}$ when ρ_0 is the self-consistent density, the linear term in the error vanishes and we are left with a quadratic approximation for the total energy error:

$$\Delta E[\rho] \approx \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \left(\frac{\delta^2 E}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right)_{\rho=\rho_0} \Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}') \quad \text{(S2)}$$

Note that as the Hartree energy is a quadratic functional of ρ, the second functional derivative corresponds to the Coulomb potential $\frac{1}{|\mathbf{r}-\mathbf{r}'|}$ for the electrostatic term of the total energy, while it is in general a functional of ρ_0 for the kinetic and exchange-correlation terms.

We report below a loose numerical test of the approximation above by plotting the error made in the prediction of the total energy of water as a function of the density error:
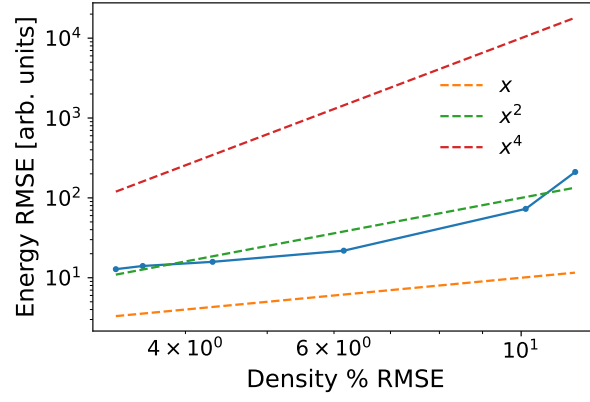
FIG. S4. (*blue line*) RMSE of the total energy prediction for $M = 2000$ as a function of the %RMSE associated with the prediction of the electron density. (*dashed lines*) linear, quadratic and quartic trend-curves.