Deep neural network for Wannier function centers

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We introduce a deep neural network (DNN) model that assigns the position of the centers of the electronic charge in the snapshots of a molecular dynamics trajectory. The electronic centers are uniquely specified by the unitary transformation that maps the occupied eigenstates onto maximally localized Wannier functions. In combination with deep potential molecular dynamics, a DNN approach to model the atomic potential energy surface at the *ab initio* density functional level of theory, the scheme makes possible to predict the dielectric properties of insulators for samples and trajectories inaccessible to direct *ab initio* simulation, without loss of accuracy. As an example, we report calculations of the infrared absorption spectra of light and heavy water at a dispersion inclusive hybrid functional level of theory, finding good agreement with experiment. Extensions to other spectroscopies, like Raman and sum frequency generation, are discussed.

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In the last decade we have witnessed a large development of machine learning (ML) schemes representing the potential energy surface (PES) of many-atom systems. These approaches are trained with first-principle data, typically from electronic density functional theory (DFT), and may boost *ab initio* molecular dynamics (AIMD) by greatly extending the accessible range of the simulations without loss of accuracy. The reduction of statistical errors resulting from larger and longer simulations leads to accurate predictions of static and dynamic properties. In addition, it becomes possible to study rare events, such as, e.g., crystal nucleation, with enhanced sampling methods in simulations of *ab initio* quality, instead of relying on numerically efficient, but less accurate, empirical force-fields.

In this context, ML approaches have focused mostly on representing the PES as a function of the nuclear coordinates. Electronic properties, accessible in AIMD, have only rarely been considered. Important examples are the polarization and/or the polarizability needed to model infrared (IR), Raman, and sum frequency generation spectra of insulators. A general formalism for the polarization utilizes maximally localized Wannier functions (MLWFs), i.e. electronic orbitals with minimal spatial spread generated by a unitary transformation of the occupied subspace within DFT. By mapping the electron density onto point charges, located at the centers (WFCs) of the MLWF density distributions, the polarization can be defined as the dipole moment of the system of electronic and nuclear point charges. For finite systems, i.e. molecules or clusters, this is the observable dipole moment, but for infinite periodic systems the dipole moment is defined modulo a quantum, and the polarization is not an observable physical property. For both finite and extended systems, however, the polarization correlation functions are physically meaningful.
and serve to describe linear response to an external perturbation.

Here we construct a deep neural network (DNN) model to represent the dependence of the WFCs on the molecular environment. The scheme, called deep WFC (DWFC), is an end-to-end model, in the sense that it does not use any ad hoc construction to go from the input atomic to the output WFC coordinates. Furthermore, the model is size extensive, preserves the symmetry of the system, and yields a polarization that varies continuously with the atomic coordinates.

In this paper, we specialize to liquid water, where the WFCs can be uniquely associated to the individual molecules, but it would be straightforward to extend the model to systems in which the WFCs can only be associated to atoms. This would be the case when water ions, such as hydronium (H$_3$O$^+$) and hydroxide (OH$^-$), are present in solution (see e.g. Ref. [24]). In these situations, interconversion of neutral molecules and ions accompanies proton transfer events, and the identity of a molecular species in an MD trajectory is not well defined. Yet, the WFCs remain unambiguously associated to the oxygen atoms.

For any insulating atomic configuration the WFCs are specified by a unitary transformation of the ground-state Kohn-Sham orbitals. We focus here on the valence electrons and use pseudopotentials to describe their interaction with the nuclei plus frozen core electrons. As expected from the principle of nearsightedness of the electronic matter [25, 26], we find that in liquid water the WFCs of a molecule depend only on the configuration of that molecule and its neighbors.

We validate the methodology by showing that DWFC and AIMD predict essentially the same molecular dipoles and WFC-atom pair correlations. For spectral calculations we combine DWFC with deep potential molecular dynamics (DPMD), an efficient ML scheme to generate nuclear trajectories of ab initio quality [9, 10]. DWFC locates the WFCs in the DPMD snapshots, giving access to the evolution of the polarization and its time correlation functions. We demonstrate this feature by calculating the IR spectra of liquid H$_2$O and D$_2$O at a hybrid functional level of theory with greatly reduced statistical errors compared to direct AIMD simulations.

In the DWFC scheme for neat water, we assign 2 hydrogens (H) and 4 WFCs to each oxygen (O) site $i$. Let $N^O_{rc} = \{j, r_{ij} < r_c\}$ be the index set of the atoms $j$ neighboring oxygen $i$ within a cutoff radius $r_c$. Atom $j$ can be either O or H. Our goal is to construct a map from the coordinates of atoms $i$ and $j$ to 12 numbers, the coordinates of 4 WFCs. The symmetry constraints here are slightly different from those considered for the PES within DPMD [9, 10]. The PES is invariant under translation, rotation, and identical particle permutation, while the WFCs are equivariant, i.e., they translate and rotate when the atomic positions are translated and rotated, guaranteeing a continuous evolution of the molecular dipoles. For this purpose we associate a local frame to each oxygen atom, $O_i$. In the local frame we sort the set $N^O_i$ in ascending order of distance from $O_i$ and specify a corresponding order for the WFCs. As shown in Fig. 1, the $i$-th local frame is defined by oxygen $O_i$ and its two nearest hydrogens, $H_{i1}$ and $H_{i2}$. The ordered local coordinate information is encoded in $D_{ij} = \{1/R_{ij}, x_{ij}/R_{ij}^2, y_{ij}/R_{ij}^2, z_{ij}/R_{ij}^2\}$, wherein $x_{ij} = x_j - x_i$, $y_{ij} = y_j - y_i$, $z_{ij} = z_j - z_i$, in terms of the Cartesian coordinates of atoms $i$ and $j$ in the local frame, $R_{ij} = \sqrt{x_{ij}^2 + y_{ij}^2 + z_{ij}^2}$, and the factor $1/R_{ij}$ reduces the weight of the more distant atoms. The set $D_{i} = \{D_{ij}, j \in N^O_i\}$ is the input of a DNN, which returns 12 numbers in output through multiple hidden layers, in each one of which the data undergo a linear transformation followed by the action of a non-linear activation function. In the final step

![FIG. 1: (Color online) Scheme of the DWFC model for WFCs in liquid water. (a) Local frame and local generalized coordinates. Atom $i$ is a generic oxygen atom and atom $j \in N^O_i$ is a generic neighbor of atom $i$. $(e_x, e_y, e_z)$ defines the local frame of atom $i$. The oxygen $i$ and the two hydrogens $H_{i1}$ and $H_{i2}$ belong to the same water molecule. We use $H_{i1}$ to denote the hydrogen that is closer to oxygen $i$. $e_x$ is parallel to the plane of the water molecule. $e_y$ is the cross product of $e_x$, $e_z$, and $e_x$. $(e_x, e_y, e_z)$ forms a local rotation matrix $U_i$ that maps the coordinates of $j$ in the laboratory frame to those in the local frame. $(x_{ij}, y_{ij}, z_{ij})$ are the Cartesian components of the vector $R_{ij}$ of length $R_{ij}$ in the local frame. The neural network input $D_{ij} = \{1/R_{ij}, x_{ij}/R_{ij}^2, y_{ij}/R_{ij}^2, z_{ij}/R_{ij}^2\}$ contains full coordinate information of atom $j$. We first sort the neighbors of atom $i$ according to their chemical species, e.g. oxygens and then hydrogens. Within each species we sort the atoms in ascending order of distances $R_{ij}$. $D_i$ denotes the sorted set of input data for site $i$. (b) Locations of the 4 WFCs, $W_{ia} (a = 1, 4)$. The DNN takes the set $D_i$ in input and gives the set $\tilde{W}_i = \{\tilde{W}_{ia}, a = 1, 4\}$ in output. The order of the four WFCs is fixed in the local frame. (c) Using the coordinates of site $i$ and the rotation matrix $U_i$, the coordinates of the WFCs are transformed to the laboratory frame.]

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\begin{align*}
D_{ij} &= \{1/R_{ij}, x_{ij}/R_{ij}^2, y_{ij}/R_{ij}^2, z_{ij}/R_{ij}^2\}, \\
D_i &= \{D_{ij}, j \in N^O_i\}, \\
W_{ia} &= \{W_{ia}, a = 1, 4\}.
\end{align*}
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from the last hidden layer to the ordered WFC positions $W_i = \{W_{i1}, W_{i2}, W_{i3}, W_{i4}\}$, only the linear transformation is applied. We call $f^\gamma$ the map $D_i \rightarrow W_i$, where $\gamma$ are the parameters of the linear transformations. We use the hyperbolic tangent for the activation function and adopt 4 hidden layers with decreasing number of nodes, i.e., 200, 100, 50, and 20 nodes, respectively, from the innermost to the outermost layer.

To apply our protocol we first identify and then order equivariantly the four WFCs associated to $O_1$. The first task is accomplished by selecting the WFCs whose distance from $O_1$ is less than 0.8 Å. The second task is accomplished by identifying $\{W_{i1}, W_{i2}, W_{i3}, W_{i4}\}$ as in Fig. 1 (b). In the local frame, $W_{i1}$ and $W_{i2}$ lie approximately along the $e_z$ axis perpendicular to the molecular plane of $O_i$, $H_{i1}$, and $H_{i2}$. $W_{i1}$ and $W_{i2}$ are lone pair centers. $W_{i3}$ and $W_{i4}$, which lie approximately along the two bonding O-H directions, are bond pair centers. To establish a unique order we assign $W_{i1}$ ($W_{i2}$) to the positive (negative) $e_z$ direction, and assign $W_{i3}$ ($W_{i4}$) to the $O_i$-$H_{i1}$ ($O_i$-$H_{i2}$) bond. In this way $f^\gamma$ is a well-defined one-to-one map in the $i$-th environment. The parameters $\gamma$ are determined by training, i.e., an optimization process that minimizes a loss function, which is here the mean square difference between the DWFC and dipole distributions for quantal (PI-DPMD) trajectories. Since only PI-AIMD trajectories were used for training, the good performance for the classical trajectory at $T = 330$ K indicates some transferability of the model to different thermodynamic conditions.

Next, we use DWFC to access the WFC evolution over long DPMD trajectories. We report in Fig. 2 the atom-WFC and dipole distributions for quantal (PI-DPMD) and classical (DPMD) 1-ns-long trajectories, at the thermodynamic conditions used to train and test the DWFC model. A comparison with two corresponding, but much shorter, AIMD trajectories shows excellent agreement in the calculated WFC distributions.

Finally, we illustrate the usefulness of the DPMD+DWFC scheme by calculating the IR absorption spectra of liquid H$_2$O and D$_2$O for a cell with 512 molecules under periodic boundary conditions. We use two microcanonical trajectories lasting 500 ps each, for H$_2$O and D$_2$O, corresponding to an average temperature of $\sim$300 K at the equilibrium density of the PI-AIMD simulation at $T = 300$ K. The frequency dependent absorption coefficient per unit length, $\alpha(\omega)$, is given by the Fourier transform of the time correlation function of the polarization $M = \sum_i \mu_i$, according to:

$$\alpha(\omega) = \frac{2\pi\omega^2\beta}{3eVn(\omega)} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle M(0) \cdot M(t) \rangle, \quad (1)$$

where $n(\omega)$ is the refractive index, which is a constant taken from experiment within the relevant frequency range, $V$ is the volume, $\beta = 1/k_BT$ is the inverse temperature, and $k_B$ is the Boltzmann factor. The calculated spectra are reported in Fig. 3 together with the corresponding experimental observations. As a further check, we calculated the variance of the spectra predicted by DNN models that differ among themselves only in the initialization of the network parameters $\gamma$. Due to the highly non-linear dependence of $f^\gamma$ on $\gamma$, different initializations result in multiple local minima in the landscape of the loss function, originating an ensemble of minimizing DNNs. The variance of the predictions within this ensemble is an intrinsic property of a DNN model and...
FIG. 2: (Color online) Distribution functions associated to the WFCs on quantum, i.e., PI, (red) and classical (blue) trajectories: (a) O-WFC pair correlation function $g_{O-WFC}(r)$; (b) H-WFC pair correlation function $g_{H-WFC}(r)$; (c) probability distribution of the magnitude for the molecular dipole ($\mu$). Solid (dashed) lines refer to DWFC (AIMD) (see text).

The small differences between theory and experiment should be attributed to the adopted DFT approximation and the use of a classical instead of a quantum auto-correlation function in Eq. 1. Ref. 43 showed that the hybrid functional PBE0 yields a substantially better IR spectrum than semilocal functionals like PBE. Our simulation used PBE0 with dispersion corrections for a better description of the liquid structure. Quantum fluctuations affect static and dynamic response of water, but while static correlations can be evaluated without approximation with path integral simulations, dynamic correlations require integrals of complex functions, whose evaluation is a major challenge for statistical simulation methods. Recently, quantum IR correlations have been calculated for water using approximate methods like ring polymer and centroid MD, indicating that quantum corrections tend to red shift the classical spectral features. Further studies of these issues will be facilitated by methods like DPMD and DWFC, which greatly improve the statistical quality of ab initio simulations.

In summary, DWFC is a powerful tool to parametrize can be used as an indicator of its accuracy. Using this criterion and a normally distributed random choice of initial parameters, we obtain a relative variance uniformly smaller than 1%, i.e., smaller than the line width of the spectra in Fig. 3.

Overall, the agreement of theory and experiment is good. The spectra are characterized by 4 main features, i.e., in order of decreasing frequencies, OH stretching, molecular bending, molecular libration, and hydrogen bond network modes (see, e.g., Ref. 37). The calculated H$_2$O spectrum is blue-shifted by $\sim$45 cm$^{-1}$ relative to experiment in the stretching region. The corresponding shift is barely noticeable in D$_2$O. Relative to experiment, the theoretical spectra of H$_2$O and D$_2$O exhibit sharper bending peaks and more intense, blue shifted, far IR features.

FIG. 3: (Color online) IR absorption spectra of H$_2$O (upper panel) and D$_2$O (lower panel). The continuous lines report DPMD+DWFC calculations (512 molecules, 0.5 ns trajectories). The variance of the spectra estimated from the DNN ensemble (see text) is smaller than the line width. The dashed lines report experimental data for H$_2$O at 298 K (Ref. 38) and for D$_2$O at 295 K (Ref. 39).
the dependence of the electronic charge centers on the atomic environment.

We recall that most ML schemes [1, 2, 8, 11], including MD studies of ferroelectric phase transitions without re-

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