Atomic scale computer simulations are now indispensable tools for solving many scientific issues, ranging from the determination of biological mechanisms to the characterization of electronic materials properties [1]. Their predictive power mainly depends on how accurately they describe the interactions between molecules. *Ab initio* (AI) simulations evaluate forces from an on-the-fly quantum chemistry calculation, generally within the framework of the density functional theory [2]. This has an appealing “hands free” aspect, but unfortunately these methods cannot yet access the time scales necessary to determine most of the material properties such as the ionic conductivity or the viscosity of liquids, let alone biological processes. This reinforces the usefulness of chemical concepts such as Lewis pairs. The localized WOs provide the missing link between electronic structure in condensed-phase and material properties.

Important efforts have been devoted to the determination of new generation FFs from AI calculations, as opposed to empirical ones, which rely on fitting to experimental data. The route from a quantum description including nuclei and electrons to a classical model of interacting molecules consists of (i) partitioning the electronic density between molecular fragments, the elementary bricks of the classical model, and (ii) computing interactions between them at the quantum level and approximating those by an analytical model. Successful steps in this direction were taken in the quantum level and approximating those by an analytical model, and (ii) computing interactions between molecular fragments, the elementary bricks of the classical model, and (ii) computing interactions between them at the quantum level and approximating those by an analytical model. The reliability of force fields is one of today’s major challenges in atomic scale computer simulations. We show how to generate predictive force fields from *ab initio* simulations in the condensed phase, using maximally localized Wannier orbitals (WO). We derive separately all interaction terms (electrostatic, exchange repulsion, dispersion, and induction) from these localized WOs. We demonstrate the excellent quality of the resulting force field for two different materials: molten salts and liquid water. This reinforces the usefulness of chemical concepts such as Lewis pairs. The localized WOs provide the missing link between electronic structure in condensed-phase and material properties.

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The paragon of such a situation is the enhanced dipole of water, and only recently the enhanced dipole of water, and only recently could a transferable FF be obtained in that case [5]. The limitations are even more severe for some ionic species which are unstable in the gas phase. This is all the more questionable, since they rely on the electronic density of the free molecule. The latter may poorly reflect the actual electronic density in the condensed system. Attributing electrons to molecules to build a coarser, classical model is not an obvious step in the condensed phase. However, the so-called maximally localized Wannier orbitals [6] (WO), based on the density functional theory (DFT) representation of electronic structure in condensed matter, provide a picture of the electron distribution which seems amenable to a chemical interpretation similar to Lewis pairs. WOs are constructed from the unitary transformation of the Kohn-Sham orbitals minimizing their spread [6]. While the Kohn-Sham orbitals are spread over the whole system, thus hindering the assignment of charge to a specific fragment, WOs have localized character. For insulating systems they decay exponentially [7] and thus have a well-defined center and a finite extent. This places the WOs at the basis of the modern theory of polarization in crystals [8]. They can be interpreted in terms of bonding orbitals or lone pairs and are intensively used to analyze the electronic structure in the condensed phase in terms of molecular properties (dipoles, quadrupoles, etc.) [9]. WOs are not only an analysis tool in terms of chemical concepts: Here we show that WOs provide the missing link between the delocalized electronic density in the condensed phase and the classical model of interacting molecules, by proposing a systematic derivation of a FF entirely from the WOs.

A realistic FF must account not only for the classical electrostatic interaction $U_{el}$, but also for three interactions arising from the quantum nature of electrons. The exchange repulsion, or van der Waals (VdW) repulsion, $U_{rep}$ is a consequence of the Pauli principle, while the dispersion (VdW attraction) $U_{disp}$ arises from correlated fluctuations of the electrons. Lastly, the induction term $U_{ind}$ reflects the distortion of the electron density in response to the electron density of a free molecule. The latter may poorly reflect the actual electronic density in the condensed system. Attributing electrons to molecules to build a coarser, classical model is not an obvious step in the condensed phase. However, the so-called maximally localized Wannier orbitals [6] (WO), based on the density functional theory (DFT) representation of electronic structure in condensed matter, provide a picture of the electron distribution which seems amenable to a chemical interpretation similar to Lewis pairs. WOs are constructed from the unitary transformation of the Kohn-Sham orbitals minimizing their spread [6]. While the Kohn-Sham orbitals are spread over the whole system, thus hindering the assignment of charge to a specific fragment, WOs have localized character. For insulating systems they decay exponentially [7] and thus have a well-defined center and a finite extent. This places the WOs at the basis of the modern theory of polarization in crystals [8]. They can be interpreted in terms of bonding orbitals or lone pairs and are intensively used to analyze the electronic structure in the condensed phase in terms of molecular properties (dipoles, quadrupoles, etc.) [9]. WOs are not only an analysis tool in terms of chemical concepts: Here we show that WOs provide the missing link between the delocalized electronic density in the condensed phase and the classical model of interacting molecules, by proposing a systematic derivation of a FF entirely from the WOs.

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electric fields, including incipient charge transfer associated with bond formation. In this work, we derive all components of the FF (referred to as Wannier Orbitals Force Field or WOFF) from the WOs. We then demonstrate the performance of this approach on a series of van der Waals, ionic, and molecular systems.

Central to our approach is an efficient partitioning of the electrons. The WOFF is based on a frozen density approximation of the localized densities associated to each species. We start with an analytical description of the WOs, that are determined from AI simulations in the condensed phase. The exponential decay of WOs suggests modeling them as Slater orbitals determined solely by their spread and center [10], which we obtain as averages over liquid configurations. Figure 1 compares the electronic density around oxygen atoms to the spherically averaged analytical result [11]. The agreement with the mean density is very good even at short distances; the scattering of the measured electronic densities is mainly due to thermal fluctuations not reproduced by the rigid density approximation. Exponential decay of the molecular density is also apparent over more than two decades and valid in the important region where the electronic densities of neighboring molecules overlap. The same type of agreement was found in all cases except for K\(^+\) for which the rate of exponential decay was not sufficiently well reproduced by our analytical expression: We resorted in that case to a simpler Slater density approximation [11].

The exchange-repulsion energy consists of two parts: kinetic and exchange-correlation. Our derivation of \(U_{\text{rep}}\), assumed to be pairwise additive, involves two approximations, namely, a frozen density ansatz and the use of a kinetic energy functional. The repulsion energy of the system is computed at the DFT level from the superposition of frozen atomic densities, \(T\) and \(\epsilon_{xc}\) the kinetic energy functional and the exchange-correlation energy density, respectively. Any form can be used for \(T\) and \(\epsilon_{xc}\), provided that the latter is the one used in the starting DFT calculations. However, the resulting \(U_{\text{rep}}\) depends on their choice. We used the LLP kinetic energy functional [14], which is generally the most accurate [13,15]. Improvements of the functionals would automatically transfer to the resulting FFs. \(U_{\text{rep}}\) generally decays as \(Be^{-a\rho}\) in the region corresponding to the first neighbor shell.

Dispersion forces are not easily captured at the DFT level. Silvestrelli showed that WOs provide a convenient framework to solve this shortcoming and introduced the computation \textit{a posteriori} of the \(-C_{ij}^{6}/r_{ij}^{6}\) interaction between Wannier centers [10], where \(C_{ij}^{6}\) depends only on the spread of the WOs [11]. These coefficients are obtained from the WOs using the expression proposed by Andersson et al. [16] for the long-range interaction between two separated fragments. We derive the dispersion term between interaction sites from the averaged sum over pairs of WOs (for \(k, l\) from different sites). Assuming an isotropic distribution of centers around the nuclei \(I, J\) at fixed distance \(d_{ij}\), we obtain to 2nd leading order \(U_{\text{disp}} = -\sum_{n=6.8}^{\infty} C_{ij}^{n}/R_{ij}^{n}\) where the dispersion coefficients are \(C_{ij}^{n} = \sum_{\ell \in I, \epsilon \in J} C_{\ell \epsilon}^{n}\) and \(C_{\ell \epsilon}^{6} = \sum_{\ell \in I, \epsilon \in J} (\ell^{2}_{\ell} + \epsilon^{2}_{\epsilon})C_{\ell \epsilon}^{6}\) [11]. The distances \(d_{ij}\) result from the orbital localization procedure and are not adjustable parameters.

Induction is included by computing molecular polarizabilities using the linear response of the WOs to an external electric field [17]. In the condensed phase special care must be taken to account for local fields created by the induced dipoles of neighboring molecules. These polarizabilities are generally smaller than in the gas phase because the electronic cloud is confined by the environment. The short-range damping function for charge-dipole interactions involves two parameters per pair of species: The damping range is chosen equal to the \(a\) parameter of the repulsion [18], and the damping strength is the only one that remains to be adjusted numerically.

WOs are finally used to derive the electrostatic interaction \(U_{el}\). They provide an efficient way to determine distributed multipoles reproducing the electrostatic potential generated by the electronic distribution around an isolated molecule [9]. Building upon the idea of Kirchner and Hüttner to use Wannier centers in conjunction with the ESP (electrostatic potential) procedure [19], we (i) compute the electrostatic potential created by an isolated molecule with its condensed-phase electronic density and (ii) determine the partial charges that best reproduce this potential in the first neighbor shell region.

We now proceed to the validation of the method on a variety of systems in which the four types of interactions

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**FIG. 1** (color online). Scatter plot of the electronic density around an O atom in a water molecule. Full line: analytical expression for the spherically averaged density; dashed line: typical nearest neighbor electronic density.
TABLE I. Properties of molten salts predicted by the WOFF: Diffusion coefficients $D_\pm$ of the ions, viscosity $\eta$, density $\rho$ (at 1 bar), electrical conductivity $\sigma$ and thermal conductivity $\Lambda$. All results are for $T = 1200$ K, except for NaF (1300 K). The agreement with experimental data [22] is very good and we provide values for data not available experimentally (NA).

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<td>0.69</td>
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<td>$\sigma$ (S · cm$^{-1}$)</td>
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<td>3.91</td>
<td>2.37</td>
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<td>$\Lambda$ (W · m$^{-1}$ · K$^{-1}$)</td>
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and measurements of their physicochemical properties are scarcer and less accurate than for classical materials. This quantitative agreement gives credibility to the use of the WOFF as a predictive tool to fill the gap in the databases that are necessary for industry.

As a first example of a molecular system, we have applied the same strategy to liquid water. Its peculiar tetrahedral structure and its numerous “anomalies” result from the subtle balance between electrostatic, VdW and induction interactions. Many FFs have been proposed to meet this modelling challenge. Here we do not aim at providing yet another one, but at illustrating the applicability of our approach. We treat water as rigid and non polarizable. WOs are now used not only for repulsion and dispersion, but also to determine the partial charges. This is a strong test of the frozen density approximation. Compared to the popular Single Point Charge SPC/E water model, the WOFF has both a stronger repulsion and larger partial charges. The average effect of induction is accounted for by the larger dipole than in the gas phase.

Figure 3 compares the radial distribution functions (rdf) for water at 1 g cm\(^{-3}\) and 303 K as obtained from the WOFF, AI simulations using the BLYP functional, and neutron scattering [23]. Our results agree very well with the experimental data, even better than the DFT initially used to build the FF. The comparatively poor performance of the latter can be traced back to the absence of long-range dispersion interactions. Their inclusion \textit{a posteriori} significantly improves the DFT results [24]. Note, however, that the rdf from AI simulations shown in Fig. 3 were obtained at a higher temperature.

FFs derived from AI simulations provide a sound alternative to empirical ones fitted to experimental data, but have been so far successful for condensed systems only when using a force-matching procedure [20]. While force matching has contributed substantial progress, the systematic derivation from the electronic density of molecules has the advantage of dramatically reducing the number of free parameters and the risk of uncontrolled compensation of errors. The key to the success of the WOFF strategy is to start from the actual electronic density in the condensed phase, and to exploit the local character of WOs in nonmetallic systems. We have established the accuracy of the resulting FF on very different systems for the prediction of both atomic scale structure and macroscopic properties. This demonstrates the central role of WOs in understanding material properties. For more complex molecules, in which anisotropy may come into play, the WOFF strategy could be adapted to derive a FF with interaction sites located on Wannier centers. One potential limitation is the extension of this “parameter-free” approach to flexible molecules, for the derivation of intramolecular terms from WOs within the frozen density approximation is not straightforward. Using the WOFF to parametrize all but these terms is nevertheless a critical step forward.