

From Localized Orbitals to Material Properties: Building Classical Force Fields for Nonmetallic Condensed Matter Systems

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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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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 is done instead *via* classical simulations, in which interactions are described by an analytical force field (FF) derived from a model. One of the major challenges remains the development of reliable FFs.

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 gas-phase [3,4]. The transferability of these gas-phase derived potentials to condensed-phase calculations is however questionable, since they rely on the electronic density of the free molecule. The latter may poorly reflect the situation in a condensed phase, where electrons feel the effect of surrounding molecules. The paragon of such a situation is 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

important since many biological, environmental, or industrial systems involve charged species.

It is therefore crucial to derive classical FFs from 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

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_{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 the rigid electronic clouds around each molecule [12,13] reconstructed from the WOs, and the resulting energy surface parametrized as a function of atomic coordinates. When WOs can be assigned to individual atoms, we introduce the spherically averaged atomic den-

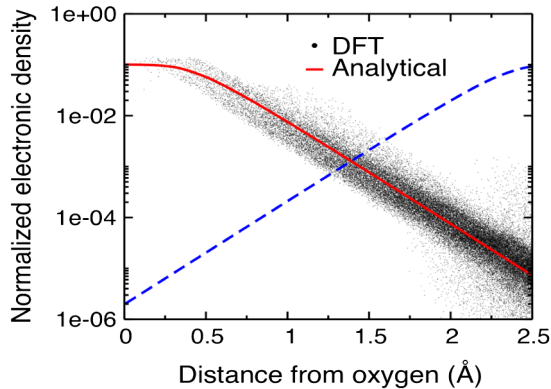


FIG. 1 (color online). Scatter plot of the electronic density around an O atom in a water molecule. Full line: analytical expression for the spherically averaged density; dashed line: typical nearest neighbor electronic density.

sity $\rho_I(r)$. U_{rep} then only depends on the interatomic separation R_{IJ} and we compute $U_{\text{rep}}(R_{IJ}) = T[\rho_s, \nabla\rho_s] + \int \epsilon_{xc}[\rho_s, \nabla\rho_s]\rho_s d^3\mathbf{r}$, where $\rho_s = \rho_I + \rho_J$ is the superposition of frozen atomic densities, T and ϵ_{xc} the kinetic energy functional and the exchange-correlation energy density, respectively. Any form can be used for T and ϵ_{xc} , provided that the latter is the one used in the starting DFT calculations. However, the resulting U_{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_{rep} generally decays as $Be^{-aR_{IJ}}$ 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 *a posteriori* of the $-C_6^{kl}/r_{kl}^6$ interaction between Wannier centers [10], where C_6^{kl} 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 $d_{k,l}$, we obtain to 2nd leading order $U_{\text{disp}} = -\sum_{n=6,8} C_n^{IJ}/R_{IJ}^n$ where the dispersion coefficients are $C_6^{IJ} = \sum_{k \in I, l \in J} C_6^{kl}$ and $C_8^{IJ} = \sum_{k \in I, l \in J} 5(d_k^2 + d_l^2)C_6^{kl}$ [11]. The distances $d_{k,l}$ 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 Hütter 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.

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

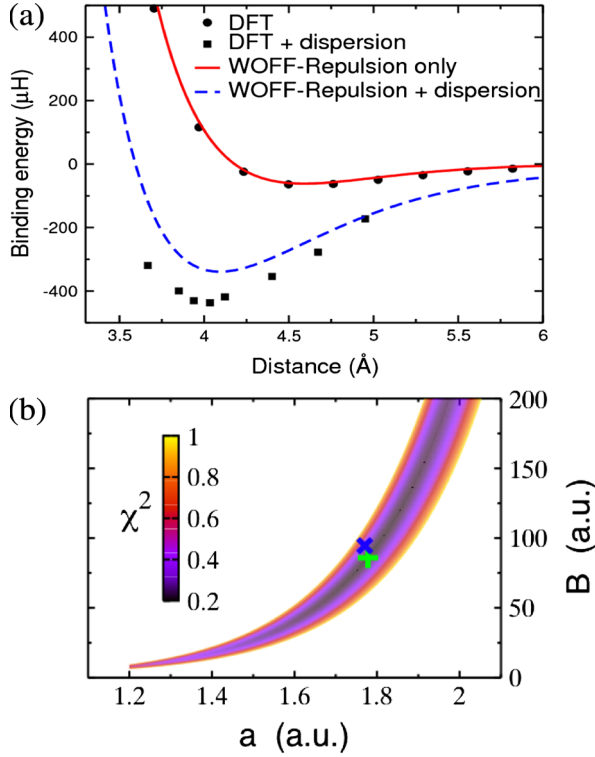


FIG. 2 (color online). (a) Binding energy of the argon dimer from the WOFF and DFT calculations (revPBE functional). The difference for dispersion comes from the orientational average over the location of the Wannier centers in the WOFF case. (b) Mean-square relative error χ^2 on the atomic forces compared to DFT (PBE functional) in the NaCl melt, as a function of the Na-Cl repulsion parameters Be^{-ar} . The set obtained by our method (x) is very close to the optimal choice (+).

differ significantly. Prior to condensed-phase systems, we tested the expressions for repulsion and dispersion interactions in the argon dimer case, for which these two terms dominate. We first determine the distance to the nucleus and spread of the WOs of an isolated argon atom by a DFT calculation using the revPBE functional, from which we compute U_{rep} and U_{disp} . The resulting pair potential is displayed in Fig. 2, with and without dispersion, together with the binding energies obtained from DFT. The agreement is almost perfect for repulsion, indicating the accu-

racy of the proposed strategy. Including the dispersion term in the WOFF reproduces well the dispersion-corrected DFT result.

The accurate description of ionic systems using a FF is much more challenging. Electrostatic and induction interactions now play an important role. In particular, the strong attraction between oppositely charged species implies a larger overlap of their electronic densities, thus questioning the validity of the frozen density approximation. An approach based on force-fitting of a polarizable ion model has already demonstrated its reliability for molten salts [20]. It requires however the numerical fitting of a large number of parameters (17 for a binary system). We applied our approach to determine the same set of parameters for a series of molten salts. Our strategy dramatically reduces (to 2) the number of free parameters and the risk of uncontrolled compensation of errors. All potentials are now determined from the WOs obtained in the *condensed phase* DFT calculations using the PBE functional. As expected, at the distance of closest approach, the repulsion energy is orders of magnitude larger than for the argon dimer.

How well are the forces on each ion reproduced by the WOFF? Figure 2 reports the overall relative error $\chi^2 = \frac{1}{N} \sum_{i=1}^N |\mathbf{F}_i^{\text{WOFF}} - \mathbf{F}_i^{\text{DFT}}|^2 / |\mathbf{F}_i^{\text{DFT}}|^2$, obtained by varying the repulsion parameters B and a for the oppositely charged NaCl pair, all remaining parameters being kept constant. The set $\{a, B\}$ provided by the WOFF approach is very close to the optimal choice. This is all the more important since the window for which this error is lower than 100% ($\chi^2 \leq 1$) is very narrow. This validates *a posteriori* the frozen density approximation for these systems. Although the value $\chi^2 = 0.363$ obtained for NaCl is the least favorable one (for the other salts, see the supplementary information [11]), it is not much larger than the value obtained with a FF of the same form but with all parameters numerically fitted ($\chi^2 = 0.118$), and significantly smaller than the one obtained with the popular Tosi-Fumi potential ($\chi^2 = 1.250$) [21]. Table I summarizes some properties of molten salts that are relevant for assessing their relative efficiency in potential heat transfer technologies, e.g., for thermal solar and nuclear power plants. For all the quantities, the agreement with experimental results is very good. Molten salts are high temperature, corrosive liquids

TABLE I. Properties of molten salts predicted by the WOFF: Diffusion coefficients D_{\pm} of the ions, viscosity η , density ρ (at 1 bar), electrical conductivity σ and thermal conductivity λ . 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).

	NaCl		KCl		NaF		KF	
	Sim	Exp	Sim	Exp	Sim	Exp	Sim	Exp
D_+ ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	9.3	10.5	10.8	10.1	6.6	NA	7.2	NA
D_- ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	6.9	8.4	9.8	9.1	5.9	NA	7.9	NA
η (cP)	1.10	0.81	0.69	0.77	1.93	1.78	1.26	1.6
ρ ($\text{g} \cdot \text{cm}^{-3}$)	1.34	1.49	1.59	1.44	1.90	1.93	2.04	1.87
σ ($\text{S} \cdot \text{cm}^{-1}$)	3.32	3.91	2.37	2.52	5.12	5.02	4.15	3.77
λ ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	0.55	0.50	0.36	0.36	1.12	NA	0.63	NA

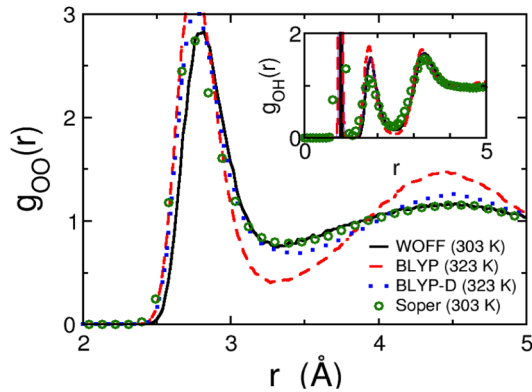


FIG. 3 (color online). rdf in water. Results are compared to neutron scattering data [23]. WOFF performs better than AI simulations, even after inclusion of empirical dispersion correction of Grimme [25].

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 $1 \text{ g} \cdot \text{cm}^{-3}$ 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 *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.

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