Behavior of polarizable models in presence of strong electric fields. I. Origin of nonlinear effects in water point-charge systems

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In the current opinion, the inclusion of polarization response in classical computer simulations is considered as one of the most important and urgent improvements to be implemented in modern empirical potential models. In this work we focus on the capability of polarizable models, based on the pairwise Coulomb interactions, to model systems where strong electric fields enter into play. As shown by Masia, Probst, and Rey (MPR) [in J. Chem. Phys. 121, 7362 (2004)], when a molecule interacts with point charges, polarizable models show underpolarization with respect to ab initio methods. We prove that this underpolarization, clearly related to nonlinear polarization effects, cannot be simply ascribed to the lack of hyperpolarization in the polarizable models, as suggested by MPR. Analysis of the electron-density rearrangement induced on a water molecule by a point charge reveals a twofold level of polarization response. One level involves intramolecular charge transfer on the whole molecular volume, with the related polarization exhibiting a seemingly linear behavior with the external electric field. The other nonlinear polarization level occurs only at strong electric fields and is found to be strictly correlated to the quantum-mechanical nature of the water molecule. The latter type of polarization has a local character, being limited to the space region of the water lone pairs. © 2005 American Institute of Physics. [DOI: 10.1063/1.2110107]

I. INTRODUCTION

In the last decade there has been a considerable effort aimed at the determination of polarizable force fields1–6 to be included in computer simulations based on empirical potentials. It is becoming widely accepted in the scientific community that polarization phenomena play an important role in shaping the intermolecular interactions in complex systems, especially when charged molecules or atomic ions are considered. Generally speaking, the polarizable models introduce a number of variational parameters that are determined by fitting molecular and/or bulk-phase properties evaluated with experiments or accurate ab initio methods. It is desirable but not necessary that these parameters have a solid theoretical background (think, e.g., to the well-known shell or Drude model7). From the practical standpoint, it is important that the polarizable force fields work reasonably well for different thermodynamical conditions (transferability between different thermodynamical environments) and for different chemical systems (transferability of the variational parameters). There have been several attempts in testing these types of transferability,2,4,5,8–10 but the results only hinted the high potentiality of the methods under study, at the same time showing the impressive amount of work to be done for obtaining a truly reliable and general polarizable force field. In particular, most polarizable force fields use a fixed set of empirical parameters to describe the nonbonded repulsive and dispersive interactions (e.g., Lennard-Jones or Buckingham potential models). Therefore, despite the above-mentioned transferability of the electrostatic interactions, the global potential preserves its reliability only for the specific thermodynamic state for which the van der Waals parameters have been determined. In fact, as shown by Badenhoop and Weinhold,11 the van der Waals radii of atoms in molecules are sensitive to the changes of the net charge on the atoms themselves. This implies that the repulsive short-range potential, arising from the electron overlap, must also depend on the net atomic charges12 and therefore from the thermodynamic state of the system. Following this concept, Chen et al.12 showed that, only supplying a polarizable force field with charge-dependent Lennard-Jones parameters, it is possible to gain a satisfactory description of the vapor-liquid densities of water. Even though some disagreement with experimental data was observed, the results by Chen et al. suggest that the parametrization of an effective force field for...
soft and extreme conditions of matter cannot actually neglect the coupling between the short-range repulsion and the polarizable part of the potential.

Besides the cited transferabilities, a second fundamental issue regarding polarizable force fields is that of assessing their response and reliability in “extreme” conditions, i.e., in the presence of strong electric fields as those generated in the surrounding of an ion or a charged group. This aspect is of key importance because most of the available polarizable schemes2,3,13,14 are based on linear response, while extreme conditions are rather common in complex systems such as biological molecules. In this respect, thorough investigations on systems involving very strong electric fields (and hence possibly nonlinear effects in the polarization response) are rare in the literature. Recently it was pointed out that in small water clusters the intermolecular charge transfer15,16 and, to a less extent, the coupling between many-body exchange and polarization,17,18 which are not accounted for in standard polarizable models, can affect significantly the polarization response (detected by polarizability or dipole moment) by a factor ranging from 10% to 20%.15 Although these studies showed interesting characteristics of water polarization when strong hydrogen-bond interactions occur, the involved electric fields are much weaker than those yielded by charged species. Regarding this last type of systems, in a recent paper19 Masia, Probst, and Rey (MPR) reported the behavior of some polarizable models in reproducing the dipole moment of water and carbon tetrachloride close to a point charge. They found that the molecular polarization is strongly underestimated by all polarizable models when the external electric field is originated by a divalent charge (or a monovalent charge for carbon tetrachloride). The authors ascribed the disagreement between ab initio and polarizable models to the hyperpolarizability, not accounted for by the latter methods. A characteristic common to all (to our knowledge) early studies on polarizable models is that the molecular quantities taken into account (e.g., charge distribution, multipole moments, polarization response, optical properties, etc.) are only indirectly related to the basic quantity underlying the macroscopic and microscopic behaviors of a system, that is the electron density. Therefore an investigation aimed at establishing the correlation existing between the electron density, as obtained from accurate quantum-mechanical calculations, and the charge-density distribution obtainable from polarizable models may provide helpful insights in clarifying the limits of the models and possibly in modeling next generations of polarizable force fields.

The aim of the present study is indeed that of investigating from the electron-density point of view the possible factors that give rise to the aforementioned underpolarization of polarizable models19 in the case of a water molecule interacting with a point charge. We remark that this underpolarization must have a basically different nature with respect to that observed in water clusters.15,16 In fact, while in water clusters intermolecular charge transfer was found15 to be the main source of underpolarization, in the charge-water system analyzed here this phenomenon cannot occur because, in the ab initio reference data, point charge does not bear wave functions. This implies that the two types of underpolarization, i.e., that generated by intermolecular charge transfer and that induced by strong electric fields, could add up in real ion-water systems, making therefore highly unreliable the global polarization response in standard polarizable models. With respect to the latter type of underpolarization, we believe that the conclusions proposed by MPR (Ref. 19) do not satisfactorily explain why underpolarization has been found significant only when a divalent point charge is taken into account, whereas it becomes negligible when a monovalent point charge is considered, no matter what is the charge-molecule distance. If hyperpolarizability were the true origin of underpolarization, as suggested by MPR, it would be reasonable to observe underpolarization also when the electric field is produced by a monovalent point charge, especially for the shortest charge-molecule distances. This was actually not observed for the case of water.

In this article we show how the electronic rearrangement (polarization) of a water molecule is affected by the electric field produced by a point charge, highlighting the contribution of the quantum-mechanical nature of the system and, in particular, of lone pairs to nonlinear effects. Consequently, we prove that a simple point dipole-based polarizable model cannot catch the essential electronic polarization of the molecule. A minimalist model for enucleating the hyperpolarizability-independent contribution from the ab initio data suggests that hyperpolarizability is not able to explain the underpolarization (given by the polarizable models) of a water molecule subject to the strong electric fields produced by a point charge. We finally show that the intramolecular electron-density reorganization of water due to the external electric field is given by the superposition of two contributions: a long-range and a short-range electron transfer, the latter associated with a sort of lone pair polarization and clearly of nonlinear nature.

II. RESULTS AND DISCUSSION

A. A general feature of polarizable models: Underpolarization

As stated in Sec. I, MPR have recently compared the performances of several polarizable models (shell,7 point dipole,3,13 and fluctuating charge20 models) to accurate ab initio data for systems made of molecules (water and carbon tetrachloride) that are in turn let to interact with monovalent and divalent positive point charges. The most important conclusions of Ref. 19 are basically two: (i) when strong electric fields enter into play, or for highly polarizable molecules, nonlinear polarization effects are fundamental for describing the molecular electronic response (the authors ascribed these effects to the hyperpolarization) and hence polarizable models based on linear response are not able to catch such effects; (ii) the comparison between different polarizable models seems to “discourage” the use of methods based on the chemical-potential equalization (CPE) principle.1,4,18 Although these statements are consistent with the data reported in the article,19 the latter conclusion is to the least questionable since an unoptimized and inaccurate CPE model20 was considered for the charge-water system, disregarding more sophisticated CPE models proposed in the recent
TABLE I. Upper part, CPE parametrization of water. $\chi$ (in eV e$^{-1}$) is the atomic electronegativity, $\eta_1$ (in eV e$^{-2}$) is the hardness of the spherical Gaussian distributions, $\eta_2$ (in eV e$^{-2}$ Å$^{-1}$) is the hardness of the dipolar Gaussian distributions, and $\alpha_0$ (in Å$^3$) is a parameter related to the polarization work. See Ref. 4 for details on the model. Lower part: properties of the isolated water molecule. $\mu$ (in D) is the dipole moment and the $\alpha_i$’s (in Å$^3$) are the components of the polarizability tensor. The molecule is placed on the $yz$ plane with the dipole moment along the $z$ direction.

<table>
<thead>
<tr>
<th></th>
<th>$\chi$</th>
<th>$\eta_1$</th>
<th>$\eta_2$</th>
<th>$\alpha_0$</th>
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</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>74.2</td>
<td>62.0</td>
<td>10.3</td>
<td>100.0</td>
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<tr>
<td>Hydrogen</td>
<td>10.0</td>
<td>120.0</td>
<td>0.0</td>
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CPE

Ab initio

$\mu$ $\alpha_{xx}$ $\alpha_{yy}$ $\alpha_{zz}$

Ab initio

$\mu$ $\alpha_{xx}$ $\alpha_{yy}$ $\alpha_{zz}$

CPE model; dotted lines, PD2-H2O model (in graphs a and b) and SH-H2O model (in graphs c and d). PDM, PD2-H2O, and SH-H2O data are taken from Ref. 19.

Very recently Paricaud et al. proposed a Gaussian charge polarizable model (GCPM) for water, based on an early model developed by Chialvo and Cummings.29 The authors showed that the GCPM can reproduce the water monomer and dimer properties and other bulk-phase data over a wide range of thermodynamic states as well. The polarizable part of the GCPM can actually be considered as a variant of the PDM.19 In fact, as PDM, the GCPM is based on the linear polarization response yielded by a single dipole localized on

C$_2$ axis with the dipole moment of water pointing away from the charge ($C_3$, configurations); (2) the point charge is placed on the axis perpendicular to the molecular plane and passing through the oxygen atom (top configurations). The dipole moment has been calculated with various polarizable models, i.e., CPE (the present one), PDM (point dipole model with a single dipole), PD2-H2O (point dipole model with three dipoles), and SH-H2O (shell model). The reference $ab$ initio data, also reported in Fig. 1, have been obtained with DFT calculations at the B3LYP/aug-cc-pVTZ level of theory. As previously stated, from Fig. 1 we see that the polarization response of the CPE model is comparable to that of other polarizable models. In particular, we notice that, while in the case of the $C_{2v}$ configurations with monovalent charge (from now on indicated as C2V-Q1 system) the $ab$ initio dipole moment is well reproduced by CPE for the long and intermediate charge-water distances [Fig. 1(a)], in the case of the $C_{2v}$ configurations with divalent charge (from now on indicated as C2V-Q2 system) underpolarization appears for charge-water distances shorter than $\sim$4 Å [Fig. 1(c)]. Underpolarization is also observable in the top configurations with both monovalent and divalent charges [Figs. 1(b) and 1(d), respectively].

The results of the comparative analysis for two charge-water configurations are reported in Fig. 1. The configurations are the following: (1) the point charge is placed on the
a point along the molecular axis toward the hydrogen atoms.\textsuperscript{30} The only remarkable difference between the GCPM and PDM is that, while polarization is shaped by a point dipole in the PDM, in the former model the induced dipole is considered to be smeared over the space for mimicking the fluctuations of the negative distributed charges [see Eq. (4) of Ref. 28]. If from one hand the GCPM has been extensively tested for several thermodynamic conditions,\textsuperscript{28} on the other hand a thorough "experimentation" regarding the polarization response under very strong electric fields has not been carried out. To this aim we have calculated the water dipole moment for the charge-water systems using the GCPM, as done for the other polarizable models (see Fig. 1). A comparison among the GCPM, PDM, and \textit{ab initio} results is reported in Fig. A1 of the auxiliary material.\textsuperscript{31} The polarization response obtained from the GCPM does not much differ from that of the PDM. We only notice that, in the case of the $C_{2v}$ configurations, the GCPM performs slightly better than the PDM, whereas the reverse occurs when the top configurations are considered.

The data shown in Figs. 1 and A1 clearly demonstrate that all considered polarizable models, including CPE, appear to be underpolarized to approximately the same extent, possibly implying that nonlinear polarization effects are not negligible for ion-water systems.

However, as we will discuss below, there are some significant differences among the various models. The CPE, PD2-H2O, and SH-H2O models agree with the \textit{ab initio} data at long and intermediate charge-water distances for the C2V-Q1 system, while the agreement is poor (underpolarization) at intermediate and short distances for the C2V-Q2 system. For the reasons discussed in Sec. I, these observations are hardly consistent with a picture that assigns the origin of the underpolarization for the C2V-Q2 system to the lack of a hyperpolarizability contribution in the models. This interpretation becomes indeed more plausible if, as done by MPR,\textsuperscript{19} one considers the behavior of the PDM, that shows underpolarization for both the C2V-Q1 and C2V-Q2 systems.

For the C2V-Q1 system [Fig. 1(a)], we see that overpolarization at very short charge-water distances for the PD2-H2O, SH-H2O, and CPE models is basically due to a damping of the \textit{ab initio} dipole moment rather than to an anomalous behavior of the models. This interpretation is strongly supported by the results of MPR which observed the same phenomenon more clearly in the case of the strongly polarizable molecule of carbon tetrachloride. In Ref. 19, such dipole moment damping was ascribed to the overlap between the molecular electronic distribution and the point charge. Indeed a similar effect, i.e., overpolarization of polarizable models at short molecule-molecule distance, was recently observed by Giese and York in the case of bifurcated water chains.\textsuperscript{17} In order to investigate and highlight the effects due to the charge-molecule overlap, we have verified (data not reported) that the CPE charge-density distribution, modeled by spherical Gaussian functions on the hydrogen and oxygen atoms and by dipolelike Gaussian functions on the oxygen atom only [see Eqs. (2) and (3) of Ref. 15], is indeed less diffuse with respect to the \textit{ab initio} electronic density. Tests using more diffuse Gaussian functions have been carried out, showing that if we allow for a significant overlap between charge-density distributions and point charge, CPE behaves similarly to the PDM for both the C2V-Q1 and C2V-Q2 systems. Similarly, the behavior of the PD2-H2O and SH-H2O models at short distances in the case of the C2V-Q1 system could be also ascribed to compensation errors related to the unrealistic lack of charge-molecule overlap and, as for the CPE model, their good agreement with the \textit{ab initio} data could be therefore fortuitous.

### B. Contribution to the water polarization from hyperpolarizability

In order to avoid possible compensation errors due to the balancing of parameters in more complex models such as PD2-H2O or CPE, and in the light of the general trend exhibited by all studied polarization methods (see Fig. 1), in the following we shall focus, as done by MPR,\textsuperscript{19} on the PDM. For the sake of clarity and simplicity of treatment, the further analysis will be only limited to the C2V-Q1 and C2V-Q2 systems.

For estimating the contribution of the first-order hyperpolarizability to the \textit{ab initio} induced dipole moment of water, the following equation, holding for a molecule subject to a uniform external electric field, has been used:

$$\mu_{ij}^{(β)} = \frac{1}{2} \sum_{j=x,y,z} \sum_{k=x,y,z} \beta_{ijk} E_i E_k, \quad (1)$$

where $\mu_{ij}^{(β)}$ is the $ith$ Cartesian component of $\mu^{(β)}$ (hyperpolarizability-induced dipole moment), $\beta_{ijk}$ is the $ijk$ component of the first-order hyperpolarizability tensor, and $E_i(E_k)$ is the $j$th($k$th) Cartesian component of the external electric field. We applied Eq. (1) to the C2V-Q1 and C2V-Q2 systems, calculating the external electric field at the nucleus position of the oxygen atom. This choice appears very reasonable considering that the oxygen atom bears most of the electron density of the water molecule. Given the point symmetry of the C2V-Q1 and C2V-Q2 systems ($C_{2v}$) and taking as $z$ axis the $C_2$ axis with the molecular dipole moment pointing in the negative $z$ direction, only the $β_{zzz}$ component of the hyperpolarizability tensor gives contribution to the induced dipole moment. For computational consistency, $β_{zzz}$ has been estimated at the B3LYP/aug-cc-pVTZ level of theory, obtaining a value of $-11.244$ au. In Fig. 2 we report the \textit{ab initio} molecular dipole moment for the C2V-Q1 and C2V-Q2 systems (thick solid lines) along with the \textit{ab initio} dipole moment subtracted by the hyperpolarizability contribution (dot-dashed lines). In principle, if hyperpolarizability were the only source of underpolarization, this hyperpolarizability-free \textit{ab initio} dipole moment should be directly comparable with that obtained by the PDM (thin solid lines). The most noticeable result obtainable from Fig. 2 is that, for long and intermediate charge-water distances (>2.5 Å), hyperpolarizability has a negligible effect in both C2V-Q1 and C2V-Q2 systems. As expected, at very short distances the hyperpolarizability contribution becomes more and more important. However, at such distances, the approximation of Eq. (1) is definitely not reliable because of the
The agreement between the hyperpolarizability-free systems and the lone pairs, we find only a marginal improvement of quite larger than that occurring between the oxygen nucleus and the lone pairs, we find only a marginal improvement of the agreement between the hyperpolarizability-free \( \mu \) dipole moments (dashed lines in Fig. 2) and those calculated with the PDM.

Also considering the better performance of the GCPM with respect to the PDM for the C2V-Q1 and C2V-Q2 systems (see Fig. A1 of the auxiliary material), the scenario depicted above is essentially preserved (see Fig. A2 of the auxiliary material). In fact, although we note a good agreement between the GCPM and hyperpolarizability-free \( \mu \) dipole moment for the C2V-Q1 system (with the external electric field calculated at the point off the oxygen atom), the results obtained for the C2V-Q2 system are still largely unsatisfactory.

In summary, these results indicate that the hyperpolarizability contribution is negligible at long and intermediate charge-water distances for both the C2V-Q1 and C2V-Q2 systems and hence its neglect in polarizable models cannot be the origin of the observed underpolarization.

**C. Electron-density polarization induced by a point charge**

Given the results reported in the previous section, we now approach the “underpolarization problem” focusing on a more subtle aspect, i.e., the rearrangement of the electron density upon application of the point-charge-generated electric field. To this end, we have calculated the charge-induced electron density, \( \Delta \rho(z) \), where the \( z \) direction coincides with the \( C_2 \) axis. \( \Delta \rho(z) \) is defined as

\[
\Delta \rho(z) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} [\rho_a(x,y,z) - \rho_b(x,y,z)] \, dx \, dy,
\]  

(2)

where \( \rho_a(x,y,z) \) and \( \rho_b(x,y,z) \) are the electron densities at \( x,y,z \) of the water molecule with and without external perturbation (point charge), respectively. The \( \Delta \rho(z) \) function is reported in Fig. 3 for the C2V-Q1 and C2V-Q2 systems and various charge-water distances. Positive values of \( \Delta \rho(z) \) indicate excess of electrons with respect to the unperturbed molecular system and vice versa. As a general feature, we notice that electron excess is located quite far from the oxygen atom \( z_\text{oxy}=0.117 \) Å; for reasons of simplicity the units of \( z \), i.e., angstroms, will not be reported in the following.

Also considering the position of the lone pairs, whose \( z \) projection is estimated to be \( z_\text{lone}=0.31 \) Å (see Ref. 32), the electron excess is still quite far from them, i.e., well above \( z=0.5 \). On the other side, electron depletion is found located beyond the \( z \) projection of the hydrogen atoms \( z_\text{hyd}=-0.469 \), i.e., outside the covalent bond region. A very interesting feature of \( \Delta \rho(z) \) is that, while the electron excess is mainly localized “outside” the molecule (\( z>0.5 \)), with a quite small contribution coming from the region of the oxygen atom (\( z<0 \)), electron depletion is spread in two well distinct regions, i.e., \( z<-0.1 \) and \( 0.2<z<0.5 \), whose contributions to the overall polarization become comparable only for strong electric fields (short charge-water distances). It is noticeable that the lone pair \( z \) projection falls precisely within the latter region. Hence one can argue that the overall charge-induced electron density \( \Delta \rho(z) \) is given by the superposition of two kinds of intramolecular electron transfer: (i) a long-range electron transfer (from \( z<-0.1 \) to \( z>0.5 \)) which persists from strong to weak electric fields, and (ii) a short-range electron transfer (from \( z>0.5 \)) which occurs only for strong electric fields. The latter type of electron transfer could be indeed associated with a sort of lone pair polarization. Another less relevant short-range electron transfer, occurring from the region beyond the hydrogen atoms to the oxygen atom, is also detectable. However, its contribution becomes comparable to the other type of short-range polarization only for weak electric fields, that is when both short-range polarizations are negligible with respect to the long-range one.

If we exclude the \( -0.1<z<0.5 \) region, we note that the...
D. A phenomenological model for extracting the classical contribution from the induced electron density

In Sec. II C we have shown that nonlinear polarization in the C2V-Q1 and C2V-Q2 systems can be attributed to the occurrence of intramolecular electron transfer involving the region of the lone pairs. For isolating a classical and linear contribution to the induced electron density from the overall polarization response, we propose here a phenomenological point dipole model (PPDM), essentially based on the behavior of \( \Delta \rho(z) \) observed in Fig. 3. As already stressed in Sec. II C, the induced electron density \( \Delta \rho(z) \) [Eq. (2)] and the dipolar Gaussian functions adopted in the CPE model have, in general, a similar behavior and this is especially true for weak external electric fields. Hence, for weak electric fields and, correspondingly, for large water-charge distances, the induced electron density can be modeled by a function of type

\[
\Delta \rho_{\text{PPDM}}(z) = A(z-z_0) \exp(-B(z-z_0)^2).
\]

We can assume that in the case of strong external perturbations, i.e., for short charge-water distances, deviation of the induced electron density from the ideal trend of Eq. (3) arises from differences between the classical and the quantum-mechanical polarization responses. Once the functional form for the PPDM has been established, we must choose a criterion/protocol for estimating the variational parameters \( A, B, \) and \( z_0 \) entering in the definition of \( \Delta \rho_{\text{PPDM}}(z) \). In the spirit of a phenomenological modeling, the parameters of \( \Delta \rho_{\text{PPDM}}(z) \) have been determined by fitting the \( \text{ab initio} \) induced electron density \( \Delta \rho(z) \) for each charge-water distance. On the other hand, given the quite large deviation of \( \Delta \rho(z) \) from the regular/ideal behavior of \( \Delta \rho_{\text{PPDM}}(z) \) at short charge-water distances (see Fig. 3), a subrange of the \( z \) space should be chosen for the fitting procedure where quantum-mechanical effects are possibly negligible. The best \( z \) range fulfilling such a requirement is certainly \( z \leq z_{\text{min}} \) where \( z_{\text{min}} \) is the \( z \) value corresponding to the minimum of \( \Delta \rho(z) \). In fact, in this range, not only \( \Delta \rho(z) \) exhibits a regular pattern as a function of the charge-water distance, but also \( z_{\text{min}} \) appears to be rather insensitive to the strength of the external perturbation. Indeed we notice that, going the charge-water distance from 7 to 2 Å, \( z_{\text{min}} \) for the C2V-Q2 system shifts by only 0.13 Å, whereas the \( z \) value corresponding to the maximum of \( \Delta \rho(z) \) shifts by about 0.46 Å. The same trend is observed for the C2V-Q1 system.

The \( \Delta \rho_{\text{PPDM}}(z) \) function has been fitted to five values of \( \Delta \rho(z) \), i.e., those corresponding to the points \( z = \frac{3}{8} z_{\text{min}}, \frac{5}{8} z_{\text{min}}, \frac{3}{8} z_{\text{min}}, \frac{7}{8} z_{\text{min}}, \frac{5}{8} z_{\text{min}}, \frac{3}{8} z_{\text{min}}, \frac{1}{8} z_{\text{min}}. \) Two constraints on the variational parameters \( A, B, \) and \( z_0 \) were imposed, thereby letting only one free parameter for the fitting. Such constraints are

\[
z_0 = 0, \quad (4)
\]

\[
\int_{-\infty}^{z_{\text{min}}} [\Delta \rho_{\text{PPDM}}(z) - \Delta \rho(z)] dz = 0. \quad (5)
\]

Equation (4) means that the dipolar Gaussian function \( \Delta \rho_{\text{PPDM}}(z) \) is centered on the molecular center of mass. This assumption is consistent with both the GCPM (Ref. 28) and PDM. They use indeed a single dipole localized on the center of mass (the GCPM) and on the \( C_2 \) axis toward the hydrogen atoms at a distance of 0.215 Å from the oxygen (the PDM). Equation (5) implies that the PPDM exactly
matches the total induced charge for \( z \leq z_{\text{min}} \). The induced electron density \( \Delta \rho(z) \) for four different charge-water distances of the C2V-Q1 system is shown in Fig. 5 along with the model behavior \( \Delta \rho_{\text{PPDM}}(z) \). In the fitting region (\( z \leq z_{\text{min}} \)) the two curves agree very well, thus supporting the assumption regarding the dipolar Gaussian-type behavior of \( \Delta \rho(z) \) in this region. In the region of electron excess (\( z > 0.5 \)) the agreement is unsatisfactory only for short charge-water distances [Figs. 5(c) and 5(d)], i.e., when lone pair polarization occurs. In particular, in Figs. 5(c) and 5(d) we observe that the polarization tail shifts far from the molecule consistently with the previously discussed picture of a twofold polarization.

Finally, in Fig. 6 we report the molecular dipole moment for the C2V-Q1 and C2V-Q2 systems calculated with the PPDM, PDM, and \textit{ab initio} method. The PPDM and \textit{ab initio} dipole moments are also compared to those obtained from the GCPM in Fig. A3 of the auxiliary material.\(^{31}\) It is noticeable that the PPDM and the PDM agree very well for long and intermediate charge-water distances, the only remarkable differences being observed at the shortest distances, i.e.,

where both the models are less reliable. When the GCPM is taken into account (Fig. A3), the agreement with the PPDM is poorer for the C2V-Q1 system, while it is very good for the C2V-Q2 system. Such features, along with Fig. 4, clearly highlight the twofold nature of the polarization response of water, with the neglect of short-range (lone pair) contribution being the main source for the observed underpolarization of polarizable models.

### III. CONCLUSIONS

Recently Masia \textit{et al.}\(^{19}\) have shown that polarizable methods based on linear polarization response exhibit underpolarization when strong electric fields, as those produced by a positive ion, are considered. The same authors speculated that the source of this underpolarization could be due to the neglect of hyperpolarizability in the studied polarizable models. In the present article we have thoroughly analyzed polarization response in charge-water systems by comparing the behavior of various polarizable models to accurate \textit{ab initio} methods. We have first generalized the statement by Masia \textit{et al.} regarding the inadequacy of linear polarizable models when strong electric fields are involved, showing that a carefully parametrized CPE model behaves similarly to the shell model or the point dipoles methodology. Then, estimating the hyperpolarizability contribution to the overall induced dipole moment by \textit{ab initio} calculations, we have shown that the neglect of hyperpolarizability is by no means responsible for the observed underpolarization phenomenon. Exploiting the symmetry of the problem, we have then computed (with \textit{ab initio} methodologies) the axial electron density induced by a point charge. With the aid of a phenomenological model aimed at reproducing the classical behavior of the induced electron density of water, it has been found that the intramolecular electron-density reorganization due to the external electric field is given by the superposition of two contributions: a long-range and a short-range electron transfer, the latter associated with a sort of lone pair polarization and clearly of nonlinear nature. This inherently quantum-mechanical effect has been found important only for strong electric fields and entirely accounts for the observed underpolarization of polarizable models. The results of the present study, which attribute to the oxygen lone pairs the origin of the underpolarization, suggest that polarizable models may behave differently in the presence of cations or anions.

Furthermore, after replacing the unpolarizable point charge with a polarizable ion, no matter what is the force field used for the modeling, one would expect a significant increase of the induced dipole moment of the system. This is certainly true also by simply considering the mutual water-ion polarization effect. However, in addition to such an effect, we would also expect a non-negligible contribution to polarization from intermolecular charge transfer, which will not be accounted for by the polarizable force field. To the light of this, it would be therefore interesting to establish the relative contribution to polarization from the two (intra- and intermolecular) charge-transfer types, and hence to establish the global limits of current linear-response-based force fields.
for modeling systems involving very strong electric fields. We are currently investigating in these directions.

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27. Throughout this paper the charge-water distance is assumed to be the charge-oxygen one.
30. Note that the point of application of the induced dipole corresponds to the molecular center of mass in the case of the GCPM, while it is slightly more shifted toward the hydrogen atoms in the PDM.
31. See EPAPS Document No. E-JCPSA6-123-521540 for the figure showing the results obtained from the Gaussian Charge Polarizable Model (GCPM). This document can be retrieved via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).