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Dynamical screening and ionic conductivity in water from *ab initio* simulations

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We present a method to calculate ionic conductivities of complex fluids from *ab initio* simulations. This is achieved by combining density functional theory molecular dynamics simulations with polarization theory. Conductivities are then obtained via a Green-Kubo formula using time-dependent effective charges of electronically screened ions. The method is applied to two different phases of warm dense water. We observe large fluctuations in the effective charges; protons can transport effective charges greater than $+e$ for ultra-short timescales. Furthermore, we compare our results with a simpler model of ionic conductivity in water that is based on diffusion coefficients. Our approach can be directly applied to study ionic conductivities of electronically insulating materials of arbitrary composition, e.g. complex molecular mixtures under such extreme conditions that occur deep inside giant planets.

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The process of electrical charge transport in water has attracted much attention since von Grotthuss [1] proposed his mechanism of correlated hydrogen jumps. Especially, *ab initio* simulations have offered new insight into the microscopic dynamical processes of proton transport and into the interaction of the several involved molecular and ionic species [2–4]. As pressure and temperature increase, the dissociation of water molecules allows more protons to contribute to the charge transport which results in a rising conductivity [5–8]. Although theoretical approaches [9–11] to calculate the electrical conductivity of water under extreme conditions can reproduce most of the experimental data well, those models require at least an assumption about the effective charge that is transported by the protons. The unscreened charge of $+e$ is a well motivated [9, 10, 12] but not the only possible choice here [11, 13].

In this work, we present an approach to obtain the electrical conductivity directly from *ab initio* simulations without making assumptions about any involved chemical species that carry defined electrical charges. To accomplish this, we combine density functional theory molecular dynamics simulations (DFT-MD) [14] with state-of-the-art polarization theory [15, 16], two well-established *ab initio* calculation techniques. The calculation of the conductivity then involves the evaluation of the Green-Kubo formula for the classical ions that carry time-dependent effective electric charges. Microscopic analyses show that large fluctuations in the effective charge of the protons occur on a femtosecond timescale that play a crucial role in the charge transport in water. Most important, the real power of the method presented here is its direct applicability to more complex systems than water, such as strongly reacting chemicals [17] and molecular mixtures in the deep inte-

rior of giant planets [13, 18].

Based on the Born-Oppenheimer approximation, our system is described by classical hydrogen ($N_H = 108$) and oxygen ions ($N_O = 54$) that are propagated with forces from the quantum-statistical treatment of the electron system with DFT. We use the exchange correlation functional of Perdew, Burke, and Ernzerhof [19] and the VASP 4.6.28 program package to perform the MD simulations [20–23]. The standard projector augmented wave (PAW) [24, 25] potentials (the 1s core electrons of oxygen are frozen) are used for the electron ion interaction with a plane-wave cutoff of 900 eV and the electronic wave functions are calculated at the Γ point. These simulation parameters have proven to yield well-converged equation of state data and diffusion coefficients [9, 10, 26]. The ion temperature is controlled with a Nosé thermostat [27], which we found not to influence the time correlation functions in test simulations.

From basic Linear Response Theory [28] follows that the electrical conductivity σ is given by a time integral over a current-current autocorrelation function,

$$\sigma = \frac{1}{3Vk_B T} \int_0^\infty dt \langle \vec{J}(t) \cdot \vec{J}(0) \rangle, \quad (1)$$

where V is the volume, $k_B T$ the thermal energy and $\vec{J}(t)$ is the total electric current of the system at time t . Equation (1) is known as the Green-Kubo formula, and it was successfully applied in, e.g., classical MD simulations to derive conductivities of molten salts [29]. In our system, the current $\vec{J}(t)$ must basically contain contributions from particles of all three different species, namely protons, oxygen nuclei, and electrons. Since the Born-Oppenheimer approximation has decoupled the motion of ions and electrons (which are treated statically at every

ionic MD step), a direct evaluation of the Green-Kubo formula is not possible because the dynamical information is lacking for the electrons. But as long as the system is non-metallic, all electronic contributions can theoretically be allocated to ions, which then carry screened effective charges instead of their bare nuclear charges.

The remaining task is now to determine the effective charge of each ion in a consistent way. The literature offers several methods to obtain effective charges from a population analysis of their surrounding electronic states [30], e.g. with a Bader analysis [31]. However, since in a MD simulation all ions are in motion, it is much more reasonable to ask which fraction of its electronic screening cloud remains attached to an ion as it is displaced from its current position. This question is adequately answered by polarization theory [15, 16], which allows us to calculate the Born effective charge tensor $\overleftrightarrow{Z}$ via the determination of the change in the electronic polarization induced by a displaced ion. The numerical procedure involves a self-consistent perturbative DFT scheme [16, 32]. For instance, this method reproduces the measured mean effective charge of +0.53 of hydrogen in liquid water [33] very well [10].

We employ VASP 5.2.8 to calculate the Born effective charge tensor $\overleftrightarrow{Z}(t)$ of every ion at each timestep of a MD run. We used a plane-wave cutoff of 400 eV and the Baldereschi point [34] in these particular calculations. This is sufficient to fulfill the charge neutrality condition $2\langle Z_H \rangle = -\langle Z_O \rangle$ for the diagonal elements within 1%. It also results in acceptable numerical costs that amount to about three times of the respective MD simulation. In all calculations the time-averaged charge tensors of both ion species are, within the statistical uncertainties, diagonal and contain the same values in any direction. This is consistent with the symmetry of the isotropic and cubic systems that we consider here.

First we examine water at a temperature of 2000 K and a density of 2 g/cm³. Under these conditions the system still retains its molecular structure but already contains about 20% of dissociated water molecules [10] so that frequent proton jumps occur. Figure 1 displays typical fluctuations of the Born effective charge of an arbitrary hydrogen and oxygen ion. Most interestingly, a hydrogen ion can carry an effective charge greater than +1 for short times. Such anomalous (anti-) screening can often be correlated with events at which the hydrogen ion changes its nearest oxygen ion, thus performing a Grotthuss-like proton jump into the respective direction. An explanation for temporarily anti-screened hydrogen ions is given by the breaking of the proton's bond to its oxygen and a jump to the next oxygen ion to form another bond again. During such a process the initial bonding electrons pull back to its oxygen ion while electronic charge density from the second oxygen ion is attracted by the incoming proton to form the new bond. This ef-

FIG. 1. (Color online) Fluctuations in the diagonal Born effective charges for a hydrogen and an oxygen ion. The triangles indicate Grotthuss-like proton jumps (changes of the proton's nearest oxygen neighbor, detectable with a geometric analysis). One timestep amounts to 0.3 fs.

fectively creates an additional negative current that is directed oppositely to the motion of the proton. Nevertheless, effective charges of +2 can occur also without a proton jump, see Fig. 1 near timestep 200. We then relate this effect to protons that have already large vibrational amplitudes but do not yet have enough kinetic energy to break their already weakened bond.

Additional simulations show that effective proton charges greater than +1 occur also in other phases of water. Figure 2 shows distributions of the Born effective charges distinguished by diagonal and off-diagonal components for both ion species in fluid and superionic water. The diagonal components are distributed over relatively broad intervals and have pronounced non-gaussian tails to high charge values. The off-diagonal components accumulate around zero. To analyze and understand the microphysics that generates such charge distributions in greater detail would go well beyond the scope of this work. Instead, we aim to put the key aspect here on the calculation of the ionic conductivity in the respective systems.

The total current $\vec{J}(t)$ in Eq. (1) is expressed as time derivative of the polarization, and is thus given by the time-dependent Born effective charge tensor via

$$\vec{J}(t) = e \sum_{i=1}^N \overleftrightarrow{Z}_i(t) \cdot \vec{v}_i(t) \quad , \quad (2)$$

where $\vec{v}_i$ is the velocity of the i -th ion and N is the total number of ions. For a simulation of 15 ps duration (50000 timesteps) at 2000 K and 2 g/cm³ we calculate the current-current correlation function $C(t) = \langle \vec{J}(t) \cdot \vec{J}(0) \rangle / 3e^2$ and the respective time integral and display the results in Figure 3. Depending on how the time-dependent charges are treated, significantly different results are obtained. In particular, the complex mecha-

FIG. 2. (Color online) Distribution of Born effective charges in partially dissociated (top) and superionic water (bottom) in arbitrary units. Solid lines represent diagonal components, dashed lines off-diagonal components. Protons are displayed in black, oxygen ions in red. The average values of the diagonal components are indicated as well.

nism of charge transfer in water does not allow us to use only constant average values of the Born effective charges, $Z_H = \langle Z_H \rangle = 0.69$ and $Z_O = \langle Z_O \rangle = -1.37$ (dashed black line). It is necessary to include their full time dependence into the correlation function to obtain converged results (full black line). Interestingly, the use of predefined constant charges can yield the same conductivity as is found with the fully time-dependent charge tensors, but only if they have values of $Z_H = 1$ and $Z_O = -2$ (blue line). The usually assumed picture of protons transporting their unscreened charges is thus not in contrast to our findings. Nevertheless, this work shows that the processes of charge transport in water involve a complex interplay of ionic movements and changes in the electronic polarization of their surrounding.

In a second simulation of 60000 timesteps we ex-

FIG. 3. (Color online) Upper: Current-current correlation function for water at 2000 K and 2 g/cm³. Depending on the treatment of the effective charges, different results are obtained, see text for further explanations. Lower: The respective time integrals of the functions from the upper figure.

amine superionic water [26, 35] at 3000 K and 3 g/cm³ and found the correlation functions to behave similarly to those shown in Figure 3. In the same way as above, constant charges of $Z_H = 1$ and $Z_O = -2$ yield the same conductivity as the time-dependent ones.

In general, the time correlations in the current-current correlation function fade on the same timescale as they do in velocity autocorrelation functions. Thereafter the time integral is stable for a certain period before statistical fluctuations take over at long times. Several 10000 timesteps are necessary to obtain converged conductivities with this method.

Furthermore, the Green-Kubo formula (1) can be decomposed into autocorrelation and crosscorrelation terms. When constant charges are assigned to all particles, the contributions from autocorrelations can be expressed by diffusion coefficients which leads to the Nernst-Einstein relation. The crosscorrelation terms contain contributions from the formation of associated species, such as water molecules, and are usually negative. Mattsson and Desjarlais [9] introduced a simple but well motivated approximation scheme for this term (originally neglecting the relatively small contribution of the oxygen ions [10]). This leads to

$$\sigma' = \frac{e^2 N_H D_H}{V k_B T} + \frac{(2e)^2 N_O D_O}{V k_B T} \left(1 - \frac{3}{2}\gamma\right), \quad (3)$$

where D_i are diffusion coefficients, which can be obtained with much less numerical effort than a reasonably converged current-current correlation function. The factor γ denotes the fraction of hydrogen ions bound to oxygen ions and has to be approximated. The term proportional to γ represents the deviation from the Nernst-Einstein relation in Eq. (3).

With such a model most of the experimental ionic conductivities [5, 7, 8] in warm dense water can be reproduced well [10]. Nevertheless, the performance of Eq. (3) can now be checked against our more general approach. For our simulations in partially dissociated and superionic water we display the results of both methods in Table I. The agreement is very good in fluid water but not in superionic water where the model of Mattsson and Desjarlais reduces to an Einstein equation for the protons ($D_O = 0$). Therefore all crosscorrelations are omitted which leads to an underestimation of the conductivity by about 50%. We checked that, although the oxygen ions themselves are immobile, correlation terms between protons and oxygen ions are important here. It is thus necessary to follow our more general approach for a quantitatively accurate description of the ionic conductivity in the superionic phase of water. Moreover, this method is directly applicable to more complex systems such as chemically reacting mixtures that contain several different ion species [13, 17, 18].

Finally, we note that the theoretical basics of our approach do not allow its application to electronically

TABLE I. Electrical conductivities from the current-current autocorrelation function (1) calculated with time-dependent Born effective charges, σ , and with constant charges of +1 for hydrogen and -2 for oxygen, $\sigma_{+1,-2}$. These are compared with those derived from equation (3), σ' (γ is taken from Ref. [10]). For additional comparison, the conductivity using Eqs. (1) and (2) with time-dependent Bader charges, σ_B , instead of Born effective charges is given as well. Bader charges [31] do not capture electronic polarization effects and should not be used to calculate conductivities. All conductivities along with estimated errors are given in $1/\Omega\text{cm}$.

T [K]	ρ [g/cm ³]	σ	$\sigma_{+1,-2}$	σ'	σ_B
2000	2.0	30 ± 3	30 ± 3	28 ± 2	11 ± 1
3000	3.0	140 ± 15	140 ± 15	91 ± 3	55 ± 5

conducting systems. However, we expect that reasonable total conductivity values can yet be obtained for matter with thermally activated electrons by treating them at nonzero temperature also in Born effective charge calculations. The electronic contribution from the Kubo-Greenwood formula usually becomes dominant quickly at higher temperatures [9, 10] and will suppress errors arising from a simultaneous inconsistency in the calculation of the Born effective charges.

In summary, we demonstrated that ionic conductivities can be calculated *ab initio* from a combination of DFT-MD simulations and polarization theory. This allows to include the electronic contribution to the current in a rigorous way when evaluating the Green-Kubo formula. The application to water reveals that the charge transfer processes involve a complex interplay between ionic motion and changes in the electronic polarization, albeit the common assumption of a proton transporting its unscreened charge of $+e$ during Grotthuss-like hopping processes is, to some extent, in line with our findings. We show that a simple conductivity model based on diffusion coefficients works well in fluid water but is not sufficient for the superionic phase. Our approach is capable of giving insight into the time-dependent mechanisms of charge transport in much more complex systems, especially in such where chemical reactions are taking place. It could furthermore aid in parameterizing continuum solvation or semi-empirical conductivity models.

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- [2] D. Marx, M. E. Tuckerman, J. Hutter, and M. Parrinello, *Nature* **397**, 601 (1999).
- [3] M. E. Tuckerman, D. Marx, and M. Parrinello, *Nature* **417**, 925 (2002).
- [4] D. Marx, *Chem. Phys. Chem.* **7**, 1848 (2006).
- [5] S. D. Hamann and M. Linton, *Trans. Faraday Soc.* **62**, 2234 (1966).
- [6] W. B. Holzapfel, *J. Chem. Phys.* **50**, 4424 (1969).
- [7] A. C. Mitchell and W. J. Nellis, *J. Chem. Phys.* **76**, 6273 (1982).
- [8] R. Chau, A. C. Mitchell, R. W. Minich, and W. J. Nellis, *J. Chem. Phys.* **114**, 1361 (2001).
- [9] T. R. Mattsson and M. P. Desjarlais, *Phys. Rev. Lett.* **97**, 017801 (2006).
- [10] M. French, T. R. Mattsson, and R. Redmer, *Phys. Rev. B* **82**, 174108 (2010).
- [11] N. Goldman, E. J. Reed, I.-F. W. Kuo, L. E. Fried, C. J. Mundy, and A. Curioni, *J. Chem. Phys.* **130**, 124517 (2009).
- [12] E. Schwegler, G. Galli, F. Gygi, and R. Q. Hood, *Phys. Rev. Lett.* **87**, 265501 (Dec 2001).
- [13] R. Chau, S. Hamel, and W. J. Nellis, *Nat. Commun.* **2**, 203 (2011).
- [14] D. Marx and J. Hutter, *Ab Initio Molecular Dynamics* (Cambridge University Press, Cambridge, 2009).
- [15] R. Resta, *Rev. Mod. Phys.* **66**, 899 (1994).
- [16] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Gianozzi, *Rev. Mod. Phys.* **73**, 515 (2001).
- [17] C. J. Wu, L. E. Fried, L. H. Yang, N. Goldman, and S. Bastea, *Nature Chemistry* **1**, 57 (2009).
- [18] M.-S. Lee and S. Scandolo, *Nat. Commun.* **2**, 185 (2011).
- [19] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (Oct 1996).
- [20] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (Jan 1993).
- [21] G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (May 1994).
- [22] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (Oct 1996).
- [23] J. Hafner, *J. Comput. Chem.* **29**, 2044 (2008).
- [24] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (Dec 1994).
- [25] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (Jan 1999).
- [26] M. French, T. R. Mattsson, N. Nettelmann, and R. Redmer, *Phys. Rev. B* **79**, 054107 (2009).
- [27] S. Nosé, *J. Chem. Phys.* **81**, 511 (1984).
- [28] R. Kubo, *J. Phys. Soc. Jpn.* **12**, 570 (1957).
- [29] J. P. Hansen and I. R. McDonald, *Phys. Rev. A* **11**, 2111 (1975).
- [30] F. Martin and H. Zipse, *J. Comput. Chem.* **26**, 97 (2005).
- [31] R. F. Bader, *Atoms in Molecules - A Quantum Theory* (Oxford University Press, Oxford, 1990).
- [32] R. W. Nunes and X. Gonze, *Phys. Rev. B* **63**, 155107 (2001).
- [33] J. Neufeind, C. J. Benmore, B. Tomberli, and P. A. Egelstaff, *J. Phys.: Condens. Matter* **14**, L429 (2002).
- [34] A. Baldereschi, *Phys. Rev. B* **7**, 5212 (1973).
- [35] C. Cavazzoni, G. L. Chiarotti, S. Scandolo, E. Tosatti, M. Bernasconi, and M. Parrinello, *Science* **283**, 44 (1999).