

Exchange-correlation functional dependence of the O 1s excitation spectrum of water

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We present a study of the sensitivity of the oxygen 1s excitation spectrum to the details of the local atomic structure of liquid water by comparing results from first principles simulations based on *ab initio* molecular dynamics runs with different exchange and correlation functionals. Even though the local atomic structure predicted by the different simulation runs differ amongst each other, a detailed analysis of the site-by-site calculated spectra always leads to the same correlations between spectral shape and local atomic structure.

Water is one of the most studied and controversial systems in molecular physics^{1,2}. The importance of the structure of water derives from the fundamental role of water in the existence of life as known to man. A general scientific consensus on the subject has remained elusive; while experiments can only provide indirect information on the atomic structure, the predictive power of molecular dynamics simulations depends on the specific interaction model. Even *ab initio* molecular dynamics (AIMD) of the liquid phase performed within density functional theory (DFT) yield different results depending on which exchange-correlation (XC) functional is used and whether dispersion is included in the model³.

The core-level excitation spectrum of water was interpreted in 2004 to carry signatures of two structural motifs: tetrahedral and chain forms⁴, which stimulated immense experimental and theoretical progress in the field alongside an engaged scientific debate that has been ongoing for over a decade². Since this assertion more than 10 years ago, X-ray excitation spectra have been routinely used for structural investigations across the full, complex phase diagram of water^{5–14}. However, due to the large number of structural degrees of freedom and the few spectral features of the oxygen K-edge, the interpretation of the spectroscopic data in terms of structural details on the atomic scale is difficult. The condensed-phase H₂O spectrum is characterized by three distinct features: the pre-edge, the main edge, and the post edge. The lack of one-to-one correspondence between local structural motifs and spectral features complicates the extraction of structural information from the spectra; recent work could obtain only coarse intensity–structure correlations due to the high statistical variation¹⁵.

Structural simulations (such as molecular dynamics) and subsequent spectral calculations have been invaluable in shedding light upon the matter by providing a direct link between the site-by-site spectral shape and the local atomic structure around the absorbing site. It is therefore timely to systematically investigate the vari-

ability inherent in the combined use of molecular dynamics simulations and spectral calculations. We do this here by comparing measured oxygen K-edge spectra of water both at ambient and supercritical conditions with spectra calculated using structures obtained from DFT-based molecular dynamics simulations employing a range of different exchange-correlation functionals.

We find that a statistical analysis of site-by-site correlation of the local atomic structure and the corresponding excitation spectrum for all exchange-correlation functionals tested leads to the same general statements about the sensitivity of the oxygen K-edge in terms of structure regardless of the functional used. By the construction of the applied analysis method, our results provide a clear measure of what structural details the oxygen K-edge spectroscopy is sensitive to. We find that in spite of any shortcomings of the molecular dynamics simulation or spectral calculations, systematic relative changes in experimentally obtained spectra can clearly be related to details of structural changes on the atomic scale.

We performed AIMD simulations for 64 water molecules in a cubic simulation cell in two thermodynamic conditions, at ambient conditions ($p = 1$ bar, $T = 300$ K, $\rho = 1.00$ g/cm³) and in the supercritical regime ($T = 673$ K, $p = 48$ MPa, $\rho = 0.54$ g/cm³). We then simulated the oxygen K-edge **non-resonant inelastic X-ray scattering** spectrum using the Bethe-Salpeter equation (BSE) approach as implemented in the OCEAN code^{16,17}. Our motivation is to investigate the difference of results from different structural simulation methods, and especially the structural interpretation they provide for spectra when a state-of-the-art spectrum calculation technique is applied. We chose five XC functionals for the AIMD: one LDA^{18–20} and four GGA (PBE²¹, BLYP^{22,23}, OLYP^{23,24}, and HCTH.407^{25,26}). We study the effect of dispersion correction for one of the cases, namely PBE, by including a semiempirical Grimme DFT-D2 correction²⁷. Although different exchange-correlation functionals were used during the molecular dynamics

simulations to obtain varying structural models for the spectral calculations, all spectra calculated based on each of these structural models were evaluated using the LDA (PW92²⁸) functional. This allows us to separate the effects on spectra due to the different atomic coordinates predicted by each functional from the effects due to different electronic structures predicted by the functionals. **All spectral simulations were carried out for a momentum transfer of $q = 3.1 \text{ \AA}^{-1}$ in order to properly compare the simulated and experimental spectra, which were measured at a momentum transfer of $q = 3.1 \text{ \AA}^{-1}$. For more information on the momentum transfer dependence of the oxygen K-edge of water, we refer to earlier work by Pylkkänen *et al.*¹⁰.**

Figure 1 presents the oxygen-oxygen and oxygen-hydrogen radial distribution functions (RDF) for the production runs performed with the 5 different XC functionals, respectively. Variation in the resulting RDFs according to the different XC-functionals is notable. Highly over-structured ambient water is obtained from simulations with LDA, after which the functionals yield less structure in the order of PBE, BLYP, HCTH.407, and OLYP. Comparison with the experimental RDFs for ambient water shows the BLYP functional to yield an O-O RDF and the HCTH functional to yield an O-H RDF that are closest to the experimental ones (taken from Ref. 29). At supercritical conditions ($T = 674 \text{ K}$, $p = 48 \text{ MPa}$), the order of the different functionals in terms of the RDF they exhibit is roughly the same as at ambient conditions, but differences among the functionals are generally smaller, apart from the RDF based on LDA, which still yields a significantly different and over-structured RDF even at these high T and high p conditions.

To characterize the results of the different AIMD simulation runs, we utilize local structural parameters such as introduced in Ref. 15 with the idea of investigating relations between different local structures and intensities in spectral **regions of interest (ROI)** from the simulations. We studied intramolecular and intermolecular structural parameters: the molecular bond angle (ϕ), the intramolecular OH bond-distance (the shorter OH distance d_{OH}^s and the longer distance d_{OH}^l), the number of oxygen atoms in the first (SS1), second (SS2), or first two (SS12) coordination shells, the number of donated ($\#don$), accepted ($\#acc$), and total ($\#tot$) number of hydrogen bonds, as well as the deviation from an angular- (Δ_a) and distance-defined (Δ_d) tetrahedrality. For a detailed definition of these parameters, we refer to Ref. 15. The average values of the parameters for the AIMD structures are reported in Table I. **The underlying idea is that finding quantitative descriptions for local structures (i.e. the structural parameters) on the one hand and a quantitative measure of how the spectral shape varies from local structure to local structure (i.e. the ROI intensities) on the other allows a straightforward correlation analysis between the two.**

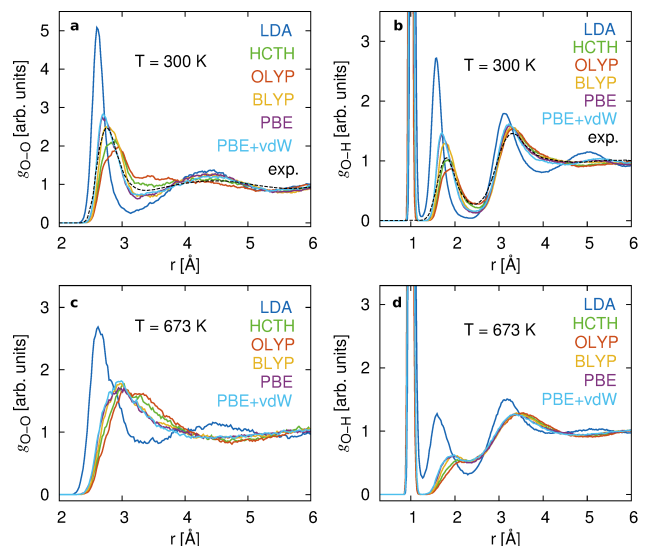


FIG. 1. Radial distribution functions of water extracted from molecular dynamics runs employing different exchange-correlation functionals. Ambient water O-O RDF (a), ambient water O-H RDF (b), supercritical water O-O RDF (c), and supercritical water O-H RDF (d). The experimental curve for ambient water was taken from Ref. 29.

Since the early days of DFT-based *ab initio* molecular dynamics simulations, it has been known that LDA yields heavily over-structured water as it overestimates the strength of hydrogen bonds resulting in H-bond distances that are too small and binding energies that are too large³⁰. Gradient-corrected XC functionals were shown to substantially improve the shortcomings of the LDA to describe weak and non-bonded interactions^{31,32}. Numerous other XC functionals have also been well characterized and benchmarked in terms of their ability to reproduce the structural and dynamic properties (both macro- and microscopic) of water³. Likewise, more elaborate and physically exact approaches, such as including intrinsic quantum effects via path-integral MD^{33–35}, hybrid functionals³⁶, functionals specifically tailored for water^{37,38}, or elaborate many-body approaches³⁹ for molecular dynamics exist. In this study we are less interested in the absolute accuracy of the specific DFT kernel or the molecular dynamics simulation regarding the description of water in the liquid state. Instead, we focus on the question of how the experimentally accessible oxygen K-edge spectrum can be related to the local atomic and electronic structure of water and changes thereof. In other words, what atomic scale structural information can be extracted from a measurement that is clearly an ensemble average over a vast number of local configurations accessible in the respective probed statistical ensemble.

Multiple options also exist for the spectral calculations once an atomic structural model has been established. One popular approach is transition potential den-

sity functional theory⁴⁰, which has been used widely and for a number of systems. However, it comes along with several pitfalls, such as the choice of treatment for the core-hole, and it usually greatly underestimates the pre- and post-edge intensity⁴¹. The BSE approach we used in the current study has been shown to reproduce all features of the oxygen K-edge for gas phase water, liquid water, and ice, and avoids explicit use of any core-hole through a Green's function formulation.^{15–17}

Figure 2 shows averages over all calculated spectra for structures obtained from the various XC functionals in comparison with experimental data measured using X-ray Raman scattering spectroscopy^{42,43}, a hard-X-ray-photon-energy-loss technique used to record excitation spectra that are free of artifacts such as saturation or self-absorption effects. The ambient spectrum was measured at the inelastic scattering beamline ID20⁴⁴ of the ESRF, France. The spectrum of water in the supercritical regime was taken from Ref. 12. The calculated averages shown in these figures represent a summation over individual oxygen K-edge spectra for all 64 oxygen atoms present in supercell structures obtained from five snapshots of each AIMD production trajectory. Thus, each spectrum presented is the average over the contributions of 320 oxygen sites. The MD snapshots were sampled at 1 ps time intervals. This was done for each temperature and each XC functional. For both thermodynamic conditions, all spectra calculated from the different MD simulation runs reasonably resemble the experimental data in that all calculated spectra show a pre-, main-, and post-edge. However, as for the RDFs of Fig. 1, a variation among the different XC kernels is evident.

Due to the use of pseudopotentials in these calculations the resulting spectra do not have a meaningful absolute energy scale. It is necessary to apply site-dependent relative chemical shifts, an alignment of the energies of the different AIMD cells, and one overall absolute shift to compare the calculated spectra to experiment. Within a single AIMD snapshot, the spectra from individual absorption sites were aligned with respect to each other by applying chemical shifts $dE_i = V_{KS}(r_i) - \frac{1}{2}W(r_i)$ where i labels the absorbing site located at r_i , V_{KS} is the total Kohn-Sham potential obtained for the AIMD snapshot in the ground-state and W is the screened core-hole potential. W is obtained through a real-space combination of many-body perturbation theory and a model dielectric function⁷. These shifts are calculated and applied automatically by the ocean code as described by Vinson *et al.*⁷. To correct for the finite size of the AIMD simulation cells we subtract from each spectrum the chemical potential of its simulation cell. After all spectra are averaged, a rigid shift is applied to the average spectrum to align the pre-edge feature to the experimentally observed energy.

Over the past decades, a consensus for generally assign-

ing the different spectral features of the oxygen K-edge has emerged. The pre-edge is generally linked to weakened or broken H-bonds and increased disorder. The main-edge has been associated with the local atomic structure in a similar way as the pre-edge. Consistent with this interpretation, supercritical water exhibits strong pre- and main-edge features¹². Moreover, the main-edge has been correlated to changes in the second shell (non-hydrogen-bonded) neighbors¹⁰. The post-edge feature is commonly related to an extended H-bond network and tetrahedral coordination, as prominent post-edge features can be found in the oxygen K-edges of the crystalline ice phases⁹.

This general assessment of the K-edge data is in line with the differences among the simulated spectra shown in Fig. 2. The spectra calculated from the MD simulation runs using the LDA XC functional show decreased pre- and greatly increased post-edge intensity as a sign of the heavily over-structured model that was already evident from the RDFs of Fig. 1. Despite this agreement about the overall interpretation of the shape of the oxygen K-edge in terms of atomic scale structure, the fine details of the interpretation of these features remain controversial and we will turn to this question next.

In our recent work we presented a method to study **correlations** between local atomic structure and spectral line intensity for core-level spectra¹⁵. In short, we defined a number of local structural parameters such as the number of donated and accepted hydrogen bonds,

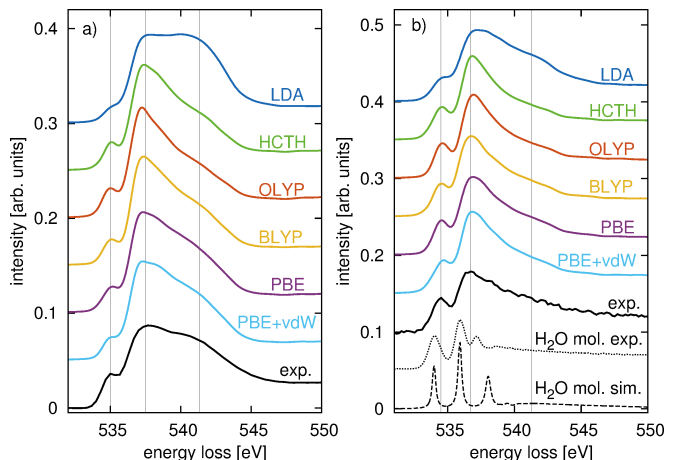


FIG. 2. XRS oxygen K-edge spectra for water from experiment (black) and AIMD simulations employing different XC functionals: ambient water (a), and supercritical ($T = 400$ °C, $p = 48$ MPa, $\rho = 0.54$ g/cm³) water (b), experiment for which was taken from 12. The shown simulation results are ergodic averages over several well separated snapshots from the respective AIMD simulation trajectories. **Part b)** also shows an experimental and a simulated spectrum of gas phase water (experimental data taken from 45 and 46).

TABLE I. Average values **and their standard deviations** for the structural parameters in the sampled snapshots. For supercritical water, intra-molecular parameters were not uniquely defined for all oxygen atoms.

Functional	ϕ	d_{OH}^s	d_{OH}^l	SS1	SS2
300 K					
LDA	105.83(5.92)	1.02(0.03)	1.06(0.03)	5.39(0.74)	17.93(2.38)
HCTH	103.81(4.87)	0.98(0.02)	1.02(0.03)	5.62(0.99)	17.77(1.85)
OLYP	102.58(5.21)	0.98(0.02)	1.01(0.02)	5.50(1.01)	17.41(2.01)
BLYP	103.91(5.13)	0.99(0.02)	1.03(0.03)	5.65(0.90)	18.04(1.80)
PBE	103.71(5.58)	1.00(0.03)	1.03(0.03)	5.45(0.95)	18.24(1.90)
PBEvdW	103.97(5.52)	1.00(0.02)	1.03(0.03)	5.53(0.90)	17.89(2.09)

Functional	SS12	#don	#acc	#tot	Δ_a	Δ_d
300 K						
LDA	23.31(2.37)	1.95(0.24)	1.95(0.37)	3.89(0.46)	97.72(37.20)	0.35(0.24)
HCTH	23.39(1.62)	1.77(0.49)	1.77(0.65)	3.54(0.89)	121.16(41.13)	0.41(0.19)
OLYP	22.91(1.76)	1.62(0.56)	1.62(0.71)	3.24(0.99)	131.51(40.72)	0.43(0.18)
BLYP	23.69(1.68)	1.88(0.35)	1.88(0.55)	3.76(0.66)	111.07(38.72)	0.38(0.19)
PBE	23.69(1.68)	1.82(0.40)	1.82(0.58)	3.63(0.77)	114.04(41.31)	0.41(0.22)
PBEvdW	23.42(1.88)	1.86(0.36)	1.86(0.54)	3.73(0.70)	114.41(40.74)	0.40(0.18)

Functional	SS1	SS2	SS12	#don	#acc	#tot	Δ_a	Δ_d
673 K								
LDA	6.30(1.41)	18.02(2.86)	24.32(3.34)	1.62(0.64)	1.53(0.79)	3.16(0.99)	151.83(44.50)	0.62(0.30)
HCTH	5.97(1.49)	17.11(2.46)	23.08(2.21)	1.09(0.72)	1.07(0.82)	2.17(1.10)	167.84(36.46)	0.60(0.28)
OLYP	5.75(1.50)	16.98(2.25)	22.73(2.19)	1.04(0.68)	1.03(0.80)	2.08(1.07)	170.75(33.39)	0.54(0.25)
BLYP	5.88(1.31)	17.18(2.30)	23.06(2.07)	1.11(0.74)	1.08(0.81)	2.19(1.10)	169.09(34.21)	0.59(0.26)
PBE	5.88(1.43)	17.63(2.45)	23.51(2.36)	1.17(0.76)	1.14(0.80)	2.31(1.18)	165.26(35.92)	0.62(0.28)
PBE vdW	5.81(1.36)	17.38(2.30)	23.18(2.11)	1.23(0.81)	1.13(0.86)	2.36(1.19)	168.07(38.35)	0.70(0.34)

and studied how these structural parameters correlate with intensities in different spectral **regions of interest** (ROI), namely the pre-, main-, and post-edge of the oxygen K-edge spectrum of water (I, [533,535.5] eV; II, [535.5,539.5] eV; III, [539.5,545] eV, see vertical lines in Fig. 2, for the centers of the regions). This recent study was performed for a single temperature and still **both analysis methods, a mean-based classification method and linear correlation coefficients between spectral (ROI) intensities and structural parameters**, readily yielded local structure – spectrum relationships established over the past decades by comparing experimental and simulation results from across the vast phase diagram of water.

The linear correlation coefficients linking structural with spectral changes for ambient water are given in Fig. 3 and for supercritical water in Fig. 4. **As in our previous work, we do not observe one-to-one correspondence between weight in the different spectral regions and structural information, but we do observe considerable correlation between the two. As such, the pre-edge intensity and a distorted local environment of the absorbing oxygen atom are positively correlated, i.e. the pre-edge intensity increases with increasing deviation from tetrahedrality and decreasing number of hydrogen bonds.** In contrast to the pre-edge, the post-edge intensity (ROI III) is positively correlated with the number of hydrogen bonds and negatively correlated with a

deviation from tetrahedrality, i.e. the post-edge is prominent if the scattering oxygen site is situated in a tetrahedrally ordered environment. The main-edge intensity (ROI II) generally correlates less with our structural parameters compared to the pre- and post-edge. Here, the intramolecular structural parameters carry most of the correlation. Even though the trends are similar in supercritical water (Fig. 4), the correlations between ROI intensities and structural parameters in the supercritical regime are generally weaker than at ambient conditions. Most importantly, we find that the correlations uncovered by our approach are largely the same regardless of the simulation details and/or XC functionals used. This has deeper implications for the information content of the oxygen K-edge of water with respect to the local atomic structure as we will elaborate in the following.

Similar structural variation results in similar spectral variations regardless of the functionals used for the structural simulation. However, this does not imply access to any quantitative, absolute interpretation of spectroscopic data in terms of structure.

Indeed, the correlations do not seem to depend greatly on the functionals used for the structural simulation, but rather on the relative and considerable statistical variation about the different ensemble averages. This implies that when it comes to the interpretation of the oxygen K-edge spectrum of water in terms of the local atomic structure, none of the probed ensembles will yield correct and reliable results as easily inferable from the difference

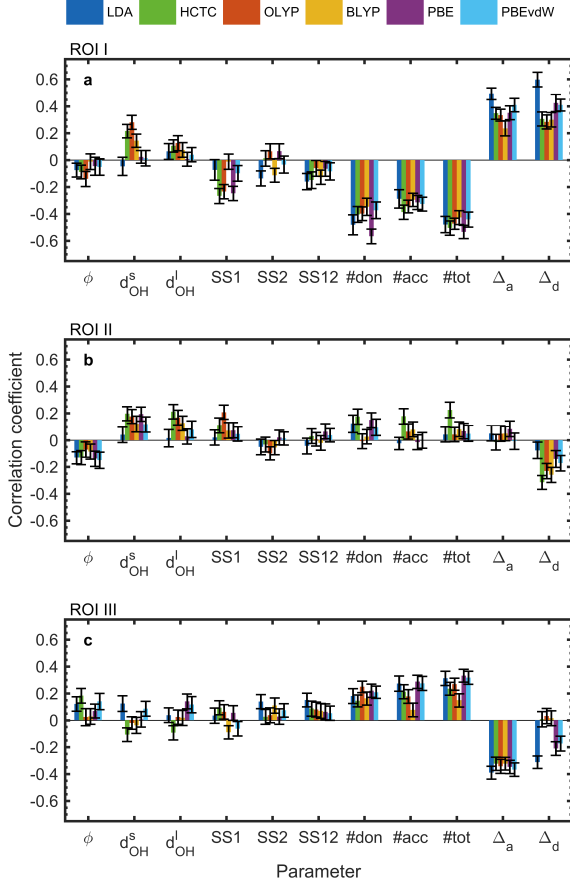


FIG. 3. Correlation coefficients between ROI intensities and the structural parameters at ambient conditions. The error limits represent the standard deviation in a 10000-fold bootstrap resampling of the original data.

between simulated and experimental radial distribution functions. Our results, however, show that observing relative trends related to structural changes are far easier to evaluate than "absolute correct" structures or their "absolute correct" spectra. Based on this work, relative changes in experimental data can precisely be related to specific structural changes in the system. This implies that systematically observed changes in spectral features in combination with a precise benchmark reference may well result in a reliable structural model.

The question whether a "hydrogen bond asymmetry" exists in water has been discussed heatedly in the literature. If it existed, this would imply a complex heterogeneous structure of liquid water, where regions of higher and lower density co-exist at ambient conditions. In view of our current results, this question seems to be desperate to answer based on the shape of the oxygen K-edge **alone**. Spectroscopic data on the oxygen K-edge carries inherently local information with considerable

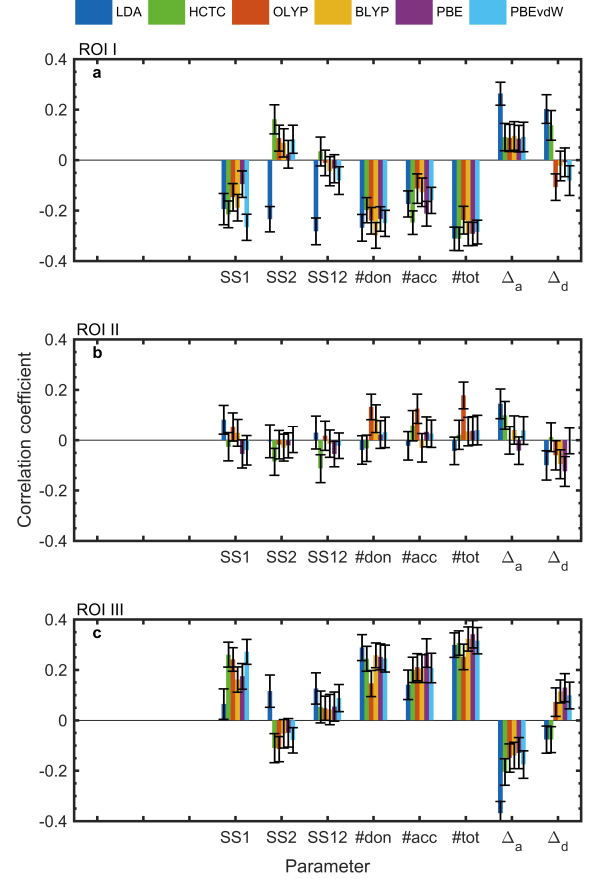


FIG. 4. Correlation coefficients between ROI intensities and the structural parameters at supercritical conditions. The error limits represent the standard deviation in a 10000-fold bootstrap resampling of the original data. The internal parameters are not defined for all water molecules and were left out.

statistical variation and we find local structures that resemble highly symmetric environments and ones that resemble highly asymmetric local environments. Due to the locality of the excitation, the shape of the oxygen K-edge, however, allows no conclusion about the spatial arrangement of these local structural motives. Moreover, the incoherent nature of O K-edge spectroscopy denies **a simple and** straightforward interpretation as to the spatial dimension of these structural distortions based on the spectral shape, but only the fact that such variation exists from one absorbing/scattering atom to another.

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- * christoph.sahle@esrf.fr
- ¹ Philip Ball, “Water: water – an enduring mystery,” *Nature* **452**, 291–292 (2008).
 - ² A. Nilsson and L. G. M. Pettersson, *Nature Communications* **6**, 8998 (2015), **And references therein**.
 - ³ Michael J. Gillan, Dario Alf , and Angelos Michaelides, “Perspective: How good is dft for water?” *The Journal of Chemical Physics* **144**, 130901 (2016).
 - ⁴ Ph. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L.  . N slund, T. K. Hirsch, L. Ojam e, P. Glatzel, L. G. M. Pettersson, and A. Nilsson, “The structure of the first coordination shell in liquid water,” *Science* **304**, 995–999 (2004), <http://science.sciencemag.org/content/304/5673/995.full.pdf>.
 - ⁵ Jared D. Smith, Christopher D. Cappa, Kevin R. Wilson, Benjamin M. Messer, Ronald C. Cohen, and Richard J. Saykally, “Energetics of hydrogen bond network rearrangements in liquid water,” *Science* **306**, 851–853 (2004), <http://science.sciencemag.org/content/306/5697/851.full.pdf>.
 - ⁶ L.- . N slund, J. Lning, Y. Ufuktepe, H. Ogasawara, Ph. Wernet, U. Bergmann, L. G. M. Pettersson, and A. Nilsson, “X-ray absorption spectroscopy measurements of liquid water,” *The Journal of Physical Chemistry B* **109**, 13835–13839 (2005), pMID: 16852732, <http://dx.doi.org/10.1021/jp052046q>.
 - ⁷ Lars-ke N slund, David C. Edwards, Philippe Wernet, Uwe Bergmann, Hirohito Ogasawara, Lars G. M. Pettersson, Satish Myneni, and Anders Nilsson, “X-ray absorption spectroscopy study of the hydrogen bond network in the bulk water of aqueous solutions,” *The Journal of Physical Chemistry A* **109**, 5995–6002 (2005), pMID: 16833935, <http://dx.doi.org/10.1021/jp050413s>.
 - ⁸ Jared D. Smith, Christopher D. Cappa, Benjamin M. Messer, Walter S. Drisdell, Ronald C. Cohen, and Richard J. Saykally, “Probing the local structure of liquid water by x-ray absorption spectroscopy,” *The Journal of Physical Chemistry B* **110**, 20038–20045 (2006), pMID: 17020392, <http://dx.doi.org/10.1021/jp063661c>.
 - ⁹ John S. Tse, Dawn M. Shaw, Dennis D. Klug, Serguei Patchkovskii, Gy rgy Vank , Giulio Monaco, and Michael Krisch, “X-ray raman spectroscopic study of water in the condensed phases,” *Phys. Rev. Lett.* **100**, 095502 (2008).
 - ¹⁰ Tuomas Pylkk nen, Valentina M. Giordano, Jean-Claude Chervin, Arto Sakko, Mikko Hakala, J. Aleksi Soininen, Keijo H m l inen, Giulio Monaco, and Simo Huotari, “Role of non-hydrogen-bonded molecules in the oxygen k-edge spectrum of ice,” *The Journal of Physical Chemistry B* **114**, 3804–3808 (2010), pMID: 20187617, <http://dx.doi.org/10.1021/jp912208v>.
 - ¹¹ Tuomas Pylkk nen, Arto Sakko, Mikko Hakala, Keijo H m l inen, Giulio Monaco, and Simo Huotari, “Temperature dependence of the near-edge spectrum of water,” *The Journal of Physical Chemistry B* **115**, 14544–14550 (2011), pMID: 22034960, <http://dx.doi.org/10.1021/jp2015462>.
 - ¹² Christoph J Sahle, Christian Sternemann, Christian Schmidt, Susi Lehtola, Sandro Jahn, Laura Simonelli, Simo Huotari, Mikko Hakala, Tuomas Pylkk nen, Alexander Nyrow, *et al.*, “Microscopic structure of water at elevated pressures and temperatures,” *Proceedings of the National Academy of Sciences* **110**, 6301–6306 (2013).
 - ¹³ Jan Meibohm, Simon Schreck, and Philippe Wernet, “Temperature dependent soft x-ray absorption spectroscopy of liquids,” *Review of Scientific Instruments* **85**, 103102 (2014), <http://dx.doi.org/10.1063/1.4896977>.
 - ¹⁴ Jonas A. Sellberg, Sarp Kaya, Vegard H. Segtnan, Chen Chen, Tolek Tyliszczak, Hirohito Ogasawara, Dennis Nordlund, Lars G. M. Pettersson, and Anders Nilsson, “Comparison of x-ray absorption spectra between water and ice: New ice data with low pre-edge absorption cross-section,” *The Journal of Chemical Physics* **141**, 034507 (2014), <http://dx.doi.org/10.1063/1.4890035>.
 - ¹⁵ Johannes Niskanen, Christoph J. Sahle, Keith Gilmore, Frank Uhlig, Jens Smiatek, and Alexander F hlisch, “Disentangling structural information from core-level excitation spectra,” *Phys. Rev. E* **96**, 013319 (2017).
 - ¹⁶ J. Vinson, J. J. Rehr, J. J. Kas, and E. L. Shirley, “Bethesalpetter equation calculations of core excitation spectra,” *Phys. Rev. B* **83**, 115106 (2011).
 - ¹⁷ K. Gilmore, John Vinson, E.L. Shirley, D. Prendergast, C.D. Pemmaraju, J.J. Kas, F.D. Vila, and J.J. Rehr, “Efficient implementation of core-excitation bethesalpetter equation calculations,” *Computer Physics Communications* **197**, 109 – 117 (2015).
 - ¹⁸ S Goedecker, M Teter, and J rg Hutter, “Separable dual-space gaussian pseudopotentials,” *Physical Review B* **54**, 1703 (1996).
 - ¹⁹ C Hartwigsen, Sephen Goedecker, and J rg Hutter, “Relativistic separable dual-space gaussian pseudopotentials from h to rn,” *Physical Review B* **58**, 3641 (1998).
 - ²⁰ M Krack, “Pseudopotentials for h to kr optimized for gradient-corrected exchange-correlation functionals,” *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta)* **114**, 145–152 (2005).
 - ²¹ JP Perdew, K Burke, and M Ernzerhof, “Generalized gradient approximation made simple,” *Physical Review Letters* **77**, 3865 (1996).
 - ²² Axel D Becke, “Density-functional exchange-energy approximation with correct asymptotic behavior,” *Physical review A* **38**, 3098 (1988).
 - ²³ Chengteh Lee, Weitao Yang, and Robert G Parr, “Development of the colle-salvetti correlation-energy formula into a functional of the electron density,” *Physical review B* **37**, 785 (1988).
 - ²⁴ Nicholas C Handy and Aron J Cohen, “Left-right correlation energy,” *Journal of Molecular Physics* **99**, 403–412 (2001).

- ²⁵ FA Hamprecht, AJ Cohen, DJ Tozer, and NC Handy, "Development and assessment of new exchange-correlation functionals," *Journal of Chemical Physics* **109**, 6264 (1998).
- ²⁶ A Daniel Boese and Nicholas C Handy, "A new parametrization of exchange-correlation generalized gradient approximation functionals," *The Journal of Chemical Physics* **114**, 5497–5503 (2001).
- ²⁷ Stefan Grimme, "Semiempirical gga-type density functional constructed with a long-range dispersion correction," *Journal of computational chemistry* **27**, 1787–1799 (2006).
- ²⁸ JP Perdew and Y Wang, "Accurate and simple analytic representation of the electron-gas correlation energy," *Physical Review B* **45**, 13244 (1992).
- ²⁹ AK Soper, "Joint structure refinement of x-ray and neutron diffraction data on disordered materials: application to liquid water," *Journal of Physics: Condensed Matter* **19**, 335206 (2007).
- ³⁰ Mark Tuckerman, Kari Laasonen, Michiel Sprik, and Michele Parrinello, "Ab initio molecular dynamics simulation of the solvation and transport of hydronium and hydroxyl ions in water," *The Journal of chemical physics* **103**, 150–161 (1995).
- ³¹ K Laasonen, F Csajka, and M Parrinello, "Water dimer properties in the gradient-corrected density functional theory," *Chemical physics letters* **194**, 172–174 (1992).
- ³² Fiona Sim, Alain St-Amant, Imre Papai, and Dennis R Salahub, "Gaussian density functional calculations on hydrogen-bonded systems," *Journal of the American Chemical Society* **114**, 4391–4400 (1992).
- ³³ Dominik Marx and Michele Parrinello, "Ab initio path integral molecular dynamics: Basic ideas," *The Journal of chemical physics* **104**, 4077–4082 (1996).
- ³⁴ Dominik Marx, Mark E Tuckerman, Jürg Hutter, and Michele Parrinello, "The nature of the hydrated excess proton in water," *Nature* **397**, 601–604 (1999).
- ³⁵ Scott Habershon, George S Fanourgakis, and David E Manolopoulos, "Comparison of path integral molecular dynamics methods for the infrared absorption spectrum of liquid water," *The Journal of chemical physics* **129**, 074501 (2008).
- ³⁶ Teodora Todorova, Ari P Seitsonen, Jürg Hutter, I-Feng W Kuo, and Christopher J Mundy, "Molecular dynamics simulation of liquid water: hybrid density functionals," *The Journal of Physical Chemistry B* **110**, 3685–3691 (2006).
- ³⁷ Aron J Cohen, Paula Mori-Sánchez, and Weitao Yang, "Insights into current limitations of density functional theory," *Science* **321**, 792–794 (2008).
- ³⁸ Michelle Fritz, Marivi Fernández-Serra, and José M Soler, "Optimization of an exchange-correlation density functional for water," *The Journal of Chemical Physics* **144**, 224101 (2016).
- ³⁹ Francesco Paesani, "Getting the right answers for the right reasons: toward predictive molecular simulations of water with many-body potential energy functions," *Accounts of Chemical Research* **49**, 1844–1851 (2016).
- ⁴⁰ Mikael Leetmaa, MP Ljungberg, Alexander Lyubartsev, Anders Nilsson, and Lars GM Pettersson, "Theoretical approximations to x-ray absorption spectroscopy of liquid water and ice," *Journal of Electron Spectroscopy and Related Phenomena* **177**, 135–157 (2010).
- ⁴¹ Thomas Fransson, Yoshihisa Harada, Nobuhiro Kosugi, Nicholas A Besley, Bernd Winter, John J Rehr, Lars GM Pettersson, and Anders Nilsson, "X-ray and electron spectroscopy of water," *Chemical reviews* **116**, 7551–7569 (2016).
- ⁴² Winfried Schülke, *Electron dynamics by inelastic X-ray scattering*, 7 (Oxford University Press, 2007).
- ⁴³ Ch J Sahle, A Mirone, J Niskanen, J Inkinen, M Krisch, and S Huotari, "Planning, performing and analyzing x-ray raman scattering experiments," *Journal of synchrotron radiation* **22**, 400–409 (2015).
- ⁴⁴ S Huotari, Ch J Sahle, Ch Henriquet, A Al-Zein, K Martel, L Simonelli, R Verbeni, H Gonzalez, M-C Lagier, C Ponchut, *et al.*, "A large-solid-angle x-ray raman scattering spectrometer at id20 of the european synchrotron radiation facility," *Journal of Synchrotron Radiation* **24** (2017).
- ⁴⁵ I Ishii, R McLaren, AP Hitchcock, and MB Robin, "Inner-shell excitations in weak-bond molecules," *The Journal of chemical physics* **87**, 4344–4360 (1987).
- ⁴⁶ AP Hitchcock and DC Mancini, "Bibliography and database of inner shell excitation spectra of gas phase atoms and molecules," *Journal of Electron Spectroscopy and Related Phenomena* **67**, vii (1994).