

Electron binding energies of water clusters: Implications for the electronic properties of liquid water

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Received 11 July 2006; in final form 31 July 2006

Available online 16 August 2006

Abstract

Green's function (GF) calculations for the valence electron binding energies of water clusters $(\text{H}_2\text{O})_{2-8}$ are reported. The results are compared with experiment for H_2O and $(\text{H}_2\text{O})_2$, and with Hartree–Fock and Kohn–Sham calculations with an exchange–correlation functional parametrized to reproduce electronic properties of the dimer. For the liquid, sequential Monte Carlo/GF calculations lead to estimates of the outermost electron binding energy (11.59 ± 0.12 eV) and of the water conduction band edge (V_0) as -0.79 ± 0.08 eV. Our predictions agree with experimental and recent theoretical results and support that the water electron affinity ($-V_0$) is smaller than the typical literature value (1.2 eV).

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1. Introduction

Water is characterized by a complex hydrogen bond network with unique properties. Some well known examples are the dependence of the density on the thermodynamic state and the water density anomaly at $T = 4$ °C [1]. The strong polarizability of liquid water, which is related to cooperative effects induced by hydrogen bonding determines its dielectric properties as well as the significant increase of the water molecule dipole moment from 1.85D in the gas to ~ 2.6 D in the liquid phase. Electronic properties of water are of fundamental importance for a better understanding of chemical reactivity in solution. However, in comparison with its energetics and structure, electronic properties of liquid water [2–9] are apparently not very well understood [9]. Of particular relevance is the relationship between hydrogen bonding and the water electronic density of states (DOS). Specifically, it is known that hydrogen bonding in water aggregates or in condensed

phases, leads to a broadening of the orbital energies (electronic broadening) and to the formation of bands. The structure of these bands is also dependent on the temperature or thermal broadening. Another fundamental aspect concerns the estimate of the water conduction band edge (V_0) or water electron affinity ($-V_0$) that has been the subject of several experimental [2,3] and theoretical investigations [10,11]. The typical literature value of V_0 is -1.2 eV [2], although some recent estimates point to a value close to zero [4]. An adequate description of the electronic structure of water is dependent on the reliable prediction of orbital energies. Therefore, the design and application of theoretical and experimental procedures for accurate estimates of electron binding energies of water aggregates and liquid water is of great interest [9].

In this Letter, we report results for the electron binding energies of water clusters based on *ab initio* Green's function (GF) or electron propagator theory (EP) [12–16]. This gives the electron binding energies as poles of the appropriate Green's function preserving the idea of orbital energies although including electron correlation effects. The one particle states are Dyson orbitals and have appropriate

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non-integer pole strengths [15]. The importance of electronic correlation effects is analyzed by comparing Green's function results with Hartree–Fock predictions. In addition, we are also reporting a comparison with Kohn–Sham (KS) orbital energies calculated with an exchange–correlation functional parametrized to reproduce the HOMO energy of the water dimer [17]. The interpretation of the (negative) KS eigenenergies as electron binding energies or ionization potentials has been widely discussed in the literature [18]. Recent works [17–19] provided indications that KS orbital energies calculated with improved exchange–correlation functionals are a better approximation to electron binding energies than are HF orbital energies via Koopmans' theorem. For liquid water, electron binding energies were estimated adopting a sequential Monte Carlo/Quantum Mechanics approach [20,21]. Using statistically uncorrelated supermolecular structures generated by Monte Carlo simulations for liquid water, GF calculations were carried out to estimate average values for the water lowest electron binding energy and electron affinity.

2. Computational details

Optimized geometries of the water clusters $(\text{H}_2\text{O})_{2-8}$ (see Fig. 1) were determined by density functional theory. The modified Perdew–Wang functional (MPW1PW91) proposed by Adamo and Barone [22] was used with the Dunning's aug-cc-pVDZ basis set [23]. For clusters with n_w water molecules we focused on the most stable conformer. Exceptions are the 6a and 6b conformers of the water hexamer ($n_w = 6$) that correspond to local minima structures. Details on the structure and energetics of the optimized clusters for $n_w = 2-7$ were previously reported [24]. The calculation of outer valence electron binding energies was carried out with the partial third-order quasiparticle theory of the electron propagator (P3) [15] as implemented in the GAUSSIAN-03 suite of programs [25]. KS orbital energies based on a exchange–correlation functional parametrized for reproducing electronic properties of the water dimer [17] are also being reported. Green's function calculations were carried out with the double augmented d-aug-cc-pVDZ basis set [26]. KS calculations were carried out with the aug-cc-pVDZ basis set.

Monte Carlo calculations for liquid water were performed with the TIP5P potential [27] in the isobaric-isothermal (npT) ensemble at $T = 298$ K and $p = 1$ atm in a cubic box with periodic boundary conditions. The number of water molecules is $n_w = 500$ and the interactions were truncated at a cutoff radius (O–O distance) of 9.0 Å. The number of steps in the production phase was 2.5×10^9 . Each step involves the attempt to move one molecule of the system.

From the configurations generated by the MC procedure, one hundred uncorrelated configurations were selected by determining a correlation step over the MC Markov chain [20,21]. Successive configurations generated

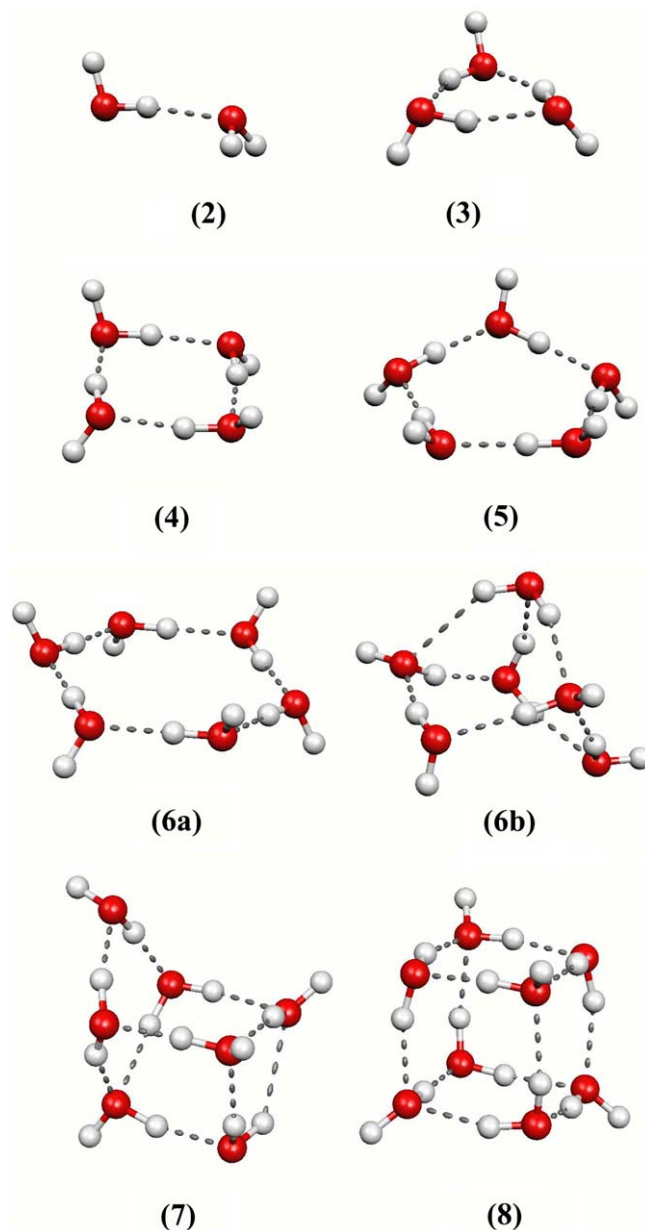


Fig. 1. Structure of water clusters $n_w = (1-8)$ from MPW1PW91/aug-cc-pVDZ optimizations. Dipole moments (in D): 1.87(1); 2.59(2); 1.13(3); 0.0(4); 1.00(5); 0(6a); 2.46(6b); 1.08(7); 0.0(8).

by the Metropolis algorithm are strongly correlated and when the property of interest involves a high computational effort, the use of uncorrelated structures is of crucial importance for evaluating averages over a relatively small number of representative configurations [20,21]. For predicting electron binding energies in liquid water, uncorrelated supermolecular structures (water clusters) including explicitly a few water ($n_w = 1-5$) molecules were selected. Surface effects were minimized by embedding the clusters in the TIP5P charge distribution of two hundred surrounding water molecules. Thus, no periodic boundary conditions were applied for evaluating electron binding energies in the liquid phase.

3. Results and discussion

Electron binding energies and electron affinities of water clusters are reported in Table 1 ($n_w = 1-5$) and Table 2 ($n_w = 6-8$). As usual, orbitals or electronic bands in water clusters or liquid phase will be labeled according to the C_{2v} symmetry species of the water monomer [9]. Comparison with experimental information is reported for the water monomer [28] and dimer [29]. For the water monomer, a good agreement is observed between P3 electron binding

Table 1
Electron binding energies and electron affinities (in eV) of water clusters (H_2O)₁₋₅

n_w	Orbital	HF	P3	KS	Experimental	
1	4a ₁	-0.203	-0.167	-0.321		
	1b ₁	13.846	12.426	11.939	12.62 ^a	
	3a ₁	15.908	14.717	14.046	14.74 ^a	
	1b ₂	19.517	18.814	17.770	18.51 ^a	
2	4a ₁	-0.142	-0.092	-0.090		
	1b ₁	13.049	11.548	11.176	11.21 ± 0.09 ^b	
	(3a ₁ ,1b ₁)	14.405	12.903	12.55		
	(3a ₁ ,1b ₁)	15.214	13.842	13.341		
	3a ₁	16.716	15.409	14.875		
	1b ₂	18.911	17.982	17.120		
	1b ₂	20.230	19.391	18.491		
3	4a ₁	-0.189	-0.145	-0.255		
	1b ₁	13.616	11.960	11.778		
	(3a ₁ ,1b ₁)	13.762	12.118	11.928		
	(3a ₁ ,1b ₁)	14.002	12.392	12.179		
	(3a ₁ ,1b ₁)	15.353	13.861	13.539		
	(3a ₁ ,1b ₁)	16.210	14.761	14.368		
	3a ₁	16.380	14.933	14.529		
	1b ₂	19.246	18.165	17.487		
	1b ₂	19.349	18.270	17.589		
	1b ₂	20.253	19.167	18.446		
4	4a ₁	-0.196	-0.154	-0.275		
	1b ₁	13.661	11.971	11.845		
	1b ₁ [2]	13.691	11.995(2)	11.877		
	1b ₁	13.700	12.045	11.926		
	(3a ₁ ,1b ₁)	14.936	13.351	13.139		
	(3a ₁ ,1b ₁)[2]	15.942	14.403	14.122		
	3a ₁	17.004	15.511	15.142		
	1b ₂	19.316	18.078	17.514		
	1b ₂ [2]	19.549	18.369	17.764		
	1b ₂	19.940	18.774	18.142		
	5	4a ₁	-0.186	-0.139	-0.242	
		1b ₁	13.505	11.784	11.692	
1b ₁		13.554	11.878	11.785		
1b ₁		13.624	11.915	11.815		
1b ₁		13.639	11.930	11.833		
(3a ₁ ,1b ₁)		13.754	12.058	11.947		
(3a ₁ ,1b ₁)		14.742	13.127	12.949		
(3a ₁ ,1b ₁)		15.478	13.906	13.686		
(3a ₁ ,1b ₁)		15.557	13.988	13.758		
3a ₁		16.776	15.271	14.941		
3a ₁		16.885	15.375	15.039		
1b ₂		19.459	18.188	17.641		
1b ₂		19.493	18.239	17.680		
1b ₂		19.521	18.281	17.729		

Numbers in italics indicate the degeneracy of the orbitals.

^a From Dutuit et al. [28].

^b From Ng et al. [29].

Table 2
Electron binding energies and electron affinities (in eV) of water clusters (H_2O)₆₋₈

n_w	Orbital	HF	P3	KS
6a	4a ₁	-0.193	-0.147	-0.255
	1b ₁	13.471	11.792	11.713
	1b ₁	13.588	11.872	11.773
	1b ₁ [2]	13.625	11.915	11.812
	1b ₁ [2]	13.629	11.911	11.820
	(3a ₁ ,1b ₁)	14.503	12.882	12.731
	(3a ₁ ,1b ₁)[2]	15.142	13.556	13.370
	3a ₁ [2]	16.515	14.979	14.688
	3a ₁	17.126	15.641	15.284
	1b ₂ [2]	19.453	18.261	17.705
	1b ₂	19.473	18.301	17.717
	6b	4a ₁	-0.145	-0.092
1b ₁		13.182	11.426	11.358
1b ₁		13.619	11.904	11.797
1b ₁		13.818	12.139	11.977
1b ₁		14.091	12.390	12.258
(3a ₁ ,1b ₁)		14.183	12.469	12.348
(3a ₁ ,1b ₁)		14.316	12.581	12.492
(3a ₁ ,1b ₁)		15.308	13.697	13.484
3a ₁		15.817	14.228	13.950
3a ₁		16.012	14.450	14.174
3a ₁		16.104	14.513	14.244
3a ₁		16.702	15.131	14.837
3a ₁		17.128	15.570	15.250
1b ₂	19.153	17.911	17.364	
1b ₂	19.323	18.129	17.530	
1b ₂	19.817	18.672	18.017	
7	4a ₁	-0.161	-0.109	-0.158
	1b ₁	13.237	11.430	11.449
	1b ₁	13.400	11.587	11.610
	1b ₁	13.430	11.692	11.669
	1b ₁	13.821	12.036	12.035
	(3a ₁ ,1b ₁)	13.999	12.215	12.205
	(3a ₁ ,1b ₁)	14.064	12.275	12.252
	(3a ₁ ,1b ₁)	14.107	12.308	12.323
	(3a ₁ ,1b ₁)	14.887	13.183	13.099
	3a ₁	15.540	13.849	13.715
	3a ₁	15.663	14.000	13.851
	3a ₁	16.045	14.417	14.256
	3a ₁	16.376	14.699	14.515
3a ₁	16.912	15.273	15.071	
3a ₁	17.244	15.564	15.349	
1b ₂	19.093	17.718	17.295	
1b ₂	19.198	17.835	17.393	
1b ₂	19.456	18.155	17.677	
1b ₂	19.498	18.221	17.709	
1b ₂	19.872	18.511	18.075	
8	4a ₁	-0.186	-0.134	-0.221
	1b ₁	13.489	11.661	11.722
	1b ₁ [2]	13.509	11.663	11.729
	1b ₁	13.600	11.797	11.846
	(3a ₁ ,1b ₁)	13.928	12.117	12.161
	(3a ₁ ,1b ₁)	13.968	12.146	12.186
	(3a ₁ ,1b ₁) [2]	13.992	12.166	12.211
	3a ₁	14.795	13.058	13.036
	3a ₁	15.676	13.905	13.844
	3a ₁ [2]	15.744	14.026	13.940
	3a ₁ [2]	16.530	14.805	14.690
	3a ₁	16.587	14.913	14.771
	3a ₁	17.607	15.875	15.693
	1b ₂ [2]	19.284	17.866	17.489
	1b ₂	19.404	18.002	17.585
	1b ₂	19.405	17.965	17.602
	1b ₂	19.986	18.605	18.186

Numbers in italics indicate the degeneracy of the orbitals.

energies and experiment. The most significant deviation from experiment is for the HOMO ($1b_1$) orbital (-0.194 eV). For the water dimer only the experimental value for the $1b_1$ orbital binding energy seems to be available [29]. In this case, the P3 approximation overestimates the HOMO binding energy by 0.338 eV. Kohn–Sham (KS) binding energies are systematically below P3 predictions for the water monomer and dimer. The agreement between the KS results and experiment for the $1b_1$ orbital reflects the fact that the exchange–correlation functional was parametrized to reproduce the HOMO energy of the water dimer [17].

Hartree–Fock electron binding energies are also reported in Table 1. They can differ significantly from P3 results illustrating the importance of relaxation and correlation energy contributions for predicting electron binding energies of water clusters. One relevant aspect characterizing the orbital energies of small water clusters is electronic broadening. This means that due to hydrogen bond interactions, splitting of the energies associated with a particular orbital energy of the water monomer is observed (see also Ref. [17] for a detailed discussion). This feature is illustrated in Fig. 2 where P3 orbital energies and their respective pole strengths for $n_w = 1, 2, 4, 6$ and 8 are reported. Electronic broadening also involves mixing of different orbitals. For the outer valence orbital presently analyzed, mixing leads to the formation of orbitals denoted by ($3a_1, 1b_1$). However, this classification is not strict for the outer valence orbitals due to electronic broadening.

If we take the P3 estimates as reference values for electron binding energies the following aspects should be stressed. HF theory overestimates electron binding energies by 1.4 – 1.8 eV. Moreover, the discrepancies between HF and P3 values for a set of N orbitals increase with increasing cluster size. This is illustrated in Fig. 3 (left panel) where we report $\delta E = \frac{1}{N} \sum_{i=1}^N \delta E_i = \frac{1}{N} \sum_{i=1}^N |E_i^{\text{HF}} - E_i^{\text{P3}}|$ as a function of the cluster size ($i = 1$ corresponds to the HOMO). By selecting electron binding energies below a given threshold

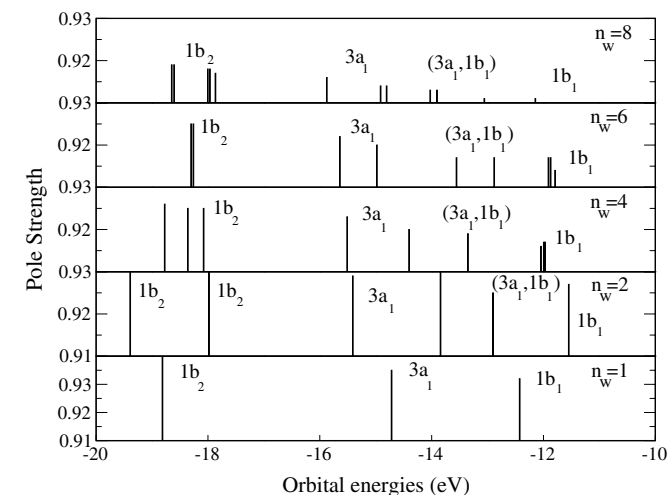


Fig. 2. Outer valence orbital energies (eV) of water clusters $((\text{H}_2\text{O})_{2-8})$, from Green's function calculations with the d-aug-cc-pVDZ basis set.

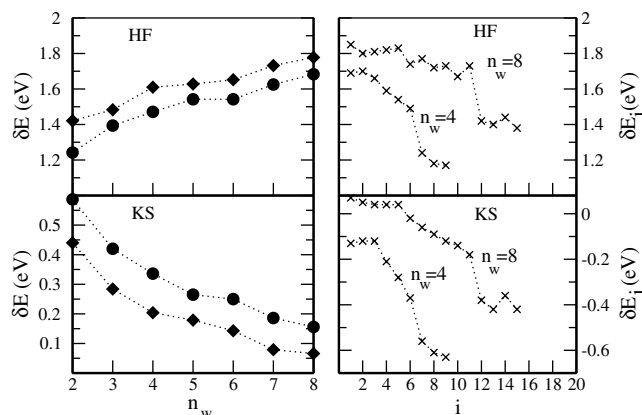


Fig. 3. Left panel: dependence of $\delta E = \frac{1}{N} \sum_{i=1}^N \delta E_i$ from HF and KS calculations on the number of water molecules n_w . Black circles: δE calculations with all the N orbitals. Black diamonds: δE calculations include only orbitals with binding energies below 16 eV (KS) and 17 eV (HF). Right panel: behavior of δE_i with the orbital number $i \in [1, N]$ ($i = 1$ is the HOMO) for HF (top) and KS (bottom) calculations.

(17 eV for HF and 16 eV for KS calculations), δE increases from 1.2 eV ($n_w = 2$) to 1.7 eV ($n_w = 8$). This behavior illustrates the importance of electronic correlation effects for predicting orbital energies of larger water aggregates. The results also suggest that deviations of HF from P3 values are more important for the outermost orbitals and then decrease with increasing electron binding energies. This is illustrated in Fig. 3 (right panel), where we report δE_i as a function of the orbital number $i \in [1, N]$ for $n_w = 4$ and $n_w = 8$.

Comparison between KS and P3 values shows that δE decreases with increasing cluster size. Deviations from the P3 values are 0.6 eV for $n_w = 2$ and 0.15 eV for $n_w = 8$. However, for electron binding energies below the 16 eV threshold (black diamonds in Fig. 3) δE is 0.45 eV ($n_w = 2$) and ~ 0.07 eV ($n_w = 8$). It is known that P3 electron binding energies are more accurate for orbitals in the outermost valence region. Therefore, the agreement between P3 and KS calculations seems to indicate that the exchange–correlation functional parametrization for the water dimer leads to improved results as the cluster size increases.

In contrast with HF results, the differences between KS and P3 results increase with increasing electron binding energies. For example, when $n_w = 3$, differences between KS and P3 electron binding energies are -0.182 , -0.190 , and -0.213 eV, for the HOMO ($1b_1$) and the HOMO–1 ($3a_1, 1b_1$) and HOMO–2 orbitals (see also the right panel of Fig. 3 for the differences when $n_w = 4$ and 8).

Hydrogen bonding in water clusters induces a shift of orbital binding energies. However, the nature (red or blue) or the magnitude of the shift exhibits some dependence on the cluster size. The following discussion will rely on P3 results. From the water monomer to the water dimer the $1b_1$ orbital binding energy is red-shifted by 0.878 eV. This red-shift is reduced to 0.466 eV for $n_w = 3$ and increases to 0.765 eV for $n_w = 8$. The $3a_1$ orbital shows a 0.692 eV

blue-shift from the monomer to the dimer reflecting the role played the $3a_1$ orbital in the energetic stabilization by hydrogen bonding, which involves mixing of the $3a_1$ and $1b_1$ orbitals. This feature will induce broadening of the $3a_1$ and $1b_1$ bands upon condensation. Although the classification of the orbitals becomes difficult with increasing cluster size due to electronic broadening, if we take the lowest electron binding energy for each band, a red-shift for the $3a_1$ orbital is observed only when $n_w > 6$. It is 1.659 eV when $n_w = 8$, and in this case, a 0.948 eV red-shift of the $1b_2$ lowest binding energy is also observed.

Experimental information on the photoemission spectra of the valence region of water clusters ($n_w \geq 20$) is available [30]. Although comparison with the present results is not direct due to differences in cluster sizes and thermal broadening, some similar trends can be observed. Specifically, downward shifts from the water monomer to the larger clusters increases up to 1.0 eV for $1b_2$, 1.12 eV for $3a_1$, and 1.05 eV for $1b_1$ [30].

Vertical electron affinities (VEAs) are also reported in Tables 1 ($n_w = 1-5$) and 2 ($n_w = 6-8$). For clusters with $n_w = 1, 3, 4, 5, 8$ and for the 6a conformer, very similar VEAs (-0.13 to -0.15 eV) are predicted. Significantly smaller values are observed for the water dimer (-0.090 eV) and hexamer 6b (-0.092 eV), and for the water heptamer (-0.109 eV). Theoretical values for adiabatic electron affinities (AEAs) of small water clusters were recently reported [31] and it is known that anionic structures are significantly different from the parent neutral structures. However, in agreement with the present results for VEAs, AEAs are negative for $n_w = 1, 3, 4, 5, 8$. This means that the corresponding anions are thermodynamically not stable. Positive AEAs are observed when $n_w = 2, 6$ and 7 [31]. This behavior is related to magic numbers in small water clusters, and reflects highly size specific electron attachment propensity [32]. Although our P3 estimates always leads to negative or small VEAs, the distinctive behavior for $n_w = 2, 6$ and 7 is in keeping with theoretical [31] and experimental works [32]. When $n_w = 6$ the dipole moments of the 6a and 6b conformers are 0 and 2.52 D, respectively (see the caption of Fig. 1). The difference between the VEAs for these two conformers (-0.147 and -0.092 eV) seems to illustrate the well known relationship between the dipole moment strength of a given species and its ability to bind an excess electron [31].

The set of valence orbital energies versus pole strengths from the Monte Carlo simulations with $n_w = 1-4$ are shown in Fig. 4. One relevant aspect illustrated in that figure is the presence of electronic as well as thermal broadening, which contributes to the mixing of $3a_1$ and $1b_1$ orbitals leading to the formation of bands. Thermal and electronic broadening in water has been discussed by Hunt et al. [5]. These authors concluded that band dispersion due to the interaction between molecules (electronic broadening) is comparable in magnitude with broadening related to local disorder (thermal broadening). Some dependence of the pole strengths on the cluster size reflects the importance

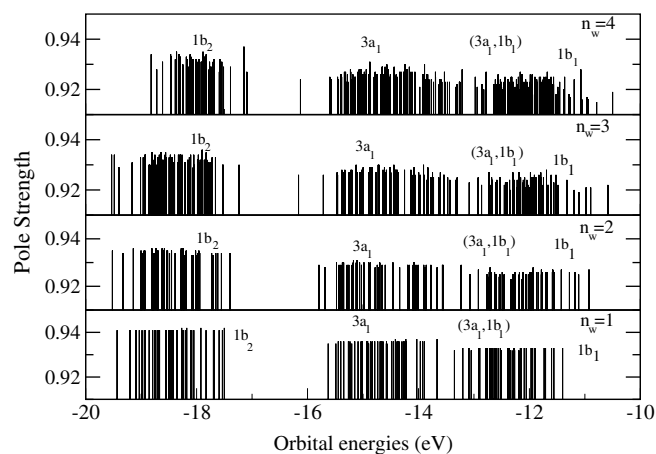


Fig. 4. Green's function orbital energies versus pole strengths in liquid water from sequential Monte Carlo/GF calculations. GF calculations were carried with the P3 method and the d-aug-cc-pVDZ basis set. One hundred uncorrelated configurations were used. The association with orbital energies with the outer valence orbitals ($3a_1$, $(3a_1, 1b_1)$, and $1b_1$) is not strict due to electronic and thermal broadening.

of correlation effects although the values are not very different from unity in comparison with inner valence electron binding energies for other systems [16]. Fig. 4 also illustrates how thermal broadening contributes to the downward shift of electron binding energies. This is simply understood considering that in contrast with the minimum-energy structures of the water clusters, at ambient temperature, a large number of liquid water configurations have lower interaction energies [33].

Table 3

Averages of the $1b_1$ electron binding energy and water conduction band edge (V_0) from sequential Monte Carlo/Green's function calculations

n_w	$1b_1^a$	$1b_1^b$	V_0
1	12.06 ± 0.05	12.06 ± 0.05	0.21 ± 0.02
2	11.77 ± 0.04	11.84 ± 0.03	0.13 ± 0.02
3	11.58 ± 0.04	11.82 ± 0.03	0.00 ± 0.02
4	11.42 ± 0.04	11.78 ± 0.03	-0.10 ± 0.02
5	11.32 ± 0.05	11.76 ± 0.03	-0.23 ± 0.02
...			
∞^c	10.75 ± 0.13	11.59 ± 0.12	-0.79 ± 0.08
Other values	10.06^d ; 9.9^e ; 10.5 ± 0.5^f	11.16 ± 0.04^g 11.57 ± 0.18^i	-1.2 ± 0.1^h -0.12^j ; -0.17 ± 0.05^k $-0.5 \leq V_0 \leq 1^l$; -0.2^m

Values in eV.

^a Average value of the HOMO.

^b Average value of the $1b_1$ band (see text for details).

^c Extrapolations were carried out by fitting the energies to the power law $a_0 + a_1 n_w^{-1} + a_2 n_w^{-2}$ ($n_w = 1$ was discarded).

^d Experimental value from Ref. [34].

^e Experimental value from Ref. [8].

^f Experimental value for ice from Ref. [35].

^g Experimental value from Winter et al. [8].

^h Experimental value from Grand et al. [2].

ⁱ Previous estimate for a cluster with $n_w = 30$ from Ref. [17].

^j From Coe et al. [3].

^k From Cabral do Couto et al. [17].

^l From Jortner [10].

^m From Henglein [11].

Table 3 reports the average values of the $1b_1$ electron binding energy and of the water conduction band edge (V_0), which is defined as the energy to take a zero kinetic energy gas phase electron to the bottom of the conduction band of the condensed phase as a delocalized or quasi-free electron [3,6]. V_0 can be associated with the average LUMO energy of liquid water and $-V_0$ is also referred as the (vertical) electron affinity of water [6].

The present results rely on sequential Monte Carlo/GF calculations including explicitly $n_w = 1-5$ water molecules. As it should be expected, the results are size dependent. The average HOMO electron binding energy is 12.06 ± 0.05 eV when the calculations are carried out with the water monomer embedded in the charge distribution of two hundred water molecules. When the calculations over one hundred uncorrelated configurations are performed with the explicit inclusion of five water molecules this value is reduced to 11.32 ± 0.05 eV. Sequential MC/GF calculations with the explicit inclusion of a larger number of water molecules are not affordable. Therefore, for estimating liquid state properties an extrapolation procedure can be considered. If it is adopted, and discarding the results for $n_w = 1$, our estimate for the HOMO average binding energy in liquid water based on embedded water clusters with $n_w = 2-5$ is 10.75 ± 0.13 eV. The average HOMO energy can be compared with the photoelectron threshold (PET) of liquid water. Our results are in good agreement with the experimental PET values [8,34,35] reported in Table 3, particularly with a value reported by Shibaguchi et al. (10.5 ± 0.5 eV) [35]. It should be observed that only the HOMO electron binding energy of each selected MC configuration was included for estimating the photoelectron threshold (PET) of liquid water. On the other hand, for each MC configuration all the orbitals associated with the $1b_1$ band will be included in the calculation of the $1b_1$ average energy (see below).

The average value of the electron binding energy associated with the $1b_1$ band can be estimated through the expression $\sum_{i=k_1}^{k_2} ps(i)E(i)/\sum_{i=k_1}^{k_2} ps(i)$, where $ps(i)$ is the pole strength of the orbital i . The values of k_1 and k_2 were defined by limiting the set of orbitals associated with $1b_1$ to the 12.4–10.0 eV interval. The choice of the lower limit was oriented by the $1b_1$ electron binding energy of the isolated water molecule (12.426 eV). These results are also reported in Table 3 for $n_w = 1-5$ and converge quickly to a limit value. The extrapolated value is 11.59 ± 0.12 eV and practically coincides with a prediction recently reported (11.57 ± 0.18 eV) [17]. This value is 0.43 eV above a recent experimental result [8]. Adopting the P3 value for $1b_1$ electron binding energy of the water molecule as reference the shift from the gas phase is 0.84 eV, which underestimates the experimental result (1.44 eV) [8] by 0.60 eV. The agreement between the present estimate of the average $1b_1$ band energy and our previous result of Ref. [17] basically reflects the fact that the $1b_1$ band energies from P3 and KS calculations are similar. Although the calculations of Ref. [17] have been carried out with a larger number of water molecules ($n_w = 30$), the results for the

average $1b_1$ band energies (Table 3) show a fast convergence with the number of water molecules.

If we take as reference the more recent experimental data for the water PET (10.06 [34] and 9.9 [8] eV), our result (10.75 ± 0.13 eV) overestimates these values by ~ 0.75 eV. A similar trend (slight overestimation of the experimental result) is observed for the average $1b_1$ band energy, which is ~ 0.45 eV above experiment. The reasons for these relatively small deviations from experiment can be related to the liquid structure predicted by the TIP5P model (simulations with other models for water could be useful) or associated with intrinsic limitations of the theoretical procedures presently adopted for estimating electron binding energies. Experimental estimates of peak widths (fwhm) for the water valence band energies were reported by Winter et al. [8]. The peak widths for the $1b_1$, $3a_1$, and $1b_2$ band were estimated as 1.45 ± 0.08 , 2.42 ± 0.10 , and 2.28 ± 0.08 eV, respectively. Although no gaussian fitting of the raw data reported in Fig. 4 was attempted, a qualitative assessment of the peak widths shows a good agreement with the experimental estimates. Specifically, in agreement with experiment, a broader $3a_1$ energy band is observed.

A slow convergence of V_0 with the number of water molecules explicitly included in the sequential MC/GF approach can be observed. Only for calculations with at least $n_w = 4$, V_0 becomes negative. The water electron affinity ($-V_0$) is related to the formation of defects, or regions where dangling hydrogen atoms can interact with a delocalized electron. This is not favored in small water clusters. If we assume that it is reasonable to extrapolate, the present prediction for V_0 is -0.79 ± 0.05 eV. Other theoretical estimates [10,11,17] are also reported in Table 3. The typical experimental value from the literature is -1.2 eV [2], although significantly smaller values (-0.2 eV [3] and ~ 0 [4]) were proposed. These results are in good agreement with the theoretical predictions of Jortner ($-0.5 \leq V_0 \leq 1$) [10], Henglein (-0.2 eV) [11], and Cabral do Couto et al (-0.17 ± 0.05 eV) [17]. In keeping with these most recent estimates, the present calculations seem to support a value smaller than the typical literature value.

4. Conclusions

Orbital binding energies of water clusters $(H_2O)_{2-8}$ were evaluated by Green's function (GF) calculations based on a partial third-order (P3) quasiparticle approximation of the electron propagator [15]. For the water monomer and dimer, P3 results were compared to experimental information. The set of results for all the clusters was also compared with HF results and values based on a parametrized exchange-correlation functional designed for reproducing electronic properties of the water dimer [17]. An overall good agreement between P3 and experimental results for the water monomer and dimer was observed. HF electron binding energies are above P3 predictions and the disagreement increases with the cluster size. KS results are in better

agreement with GF calculations. Interestingly, the agreement improves when the size of the aggregates, or the number of water molecules (n_w) increases. Sequential MC/GF calculations over one hundred uncorrelated configurations including a few water molecules ($n_w = 1-5$) embedded in the charge distribution of two hundred water molecules were carried out and the results provided estimates for the average values of the HOMO and LUMO energies in the liquid. Our prediction for the average $1b_1$ electron binding energy (11.59 ± 0.12 eV) practically coincides with a recent estimate (11.57 ± 0.18) relying on KS orbital energies [17]. The average LUMO energy can be associated with the conduction band edge (V_0) of liquid water. The present estimate for V_0 is in line with experimental and other theoretical results and supports the view [3] that the water electron affinity ($-V_0$) is smaller than the typical literature value (1.2 eV). However, although our results for electronic properties of liquid water are in keeping with other values from the literature, the strong size dependence of V_0 , and the significant computational demands of the MC/GF approach for evaluating energies of virtual orbitals [15] seems to favor the adoption of other complementary procedures for investigating electronic properties in condensed phase. This conclusion is apparently supported by the overall good agreement between KS and GF results for electron binding energies of water clusters.

Acknowledgements

This work was partially supported by CNPq and FAPESP (Brazil) and by Fundação para a Ciência e a Tecnologia (FCT), Portugal (Grant No. POCTI/43315/QUI/2001). P.C.C. gratefully acknowledges the FCT. (Ph.D. grant SFRH/XXI/BD/6503/2001).

References

- [1] G. Franzese, H.E. Stanley, *Physica A* 314 (2002) 508.
- [2] D. Grand, A. Bernas, E. Amouyal, *Chem. Phys.* 44 (1979) 73.
- [3] J.V. Coe, A.D. Earhart, M.H. Cohen, G.J. Hoffman, H.W. Sarkas, K.H. Bowen, *J. Chem. Phys.* 107 (1997) 6023.
- [4] J.V. Coe, *Int. Rev. Phys. Chem.* 20 (2001) 33.
- [5] P. Hunt, M. Sprik, R. Vuilleumier, *Chem. Phys. Lett.* 376 (2003) 68.
- [6] P. Han, D.M. Bartels, *J. Phys. Chem.* 94 (1990) 5824.
- [7] A. Bernas, C. Ferradini, J.-P. Jay-Gerin, *Chem. Phys.* 222 (1997) 151.
- [8] B. Winter, R. Weber, W. Widdra, M. Dittmar, M. Faubel, I.V. Hertel, *J. Phys. Chem. A* 108 (2004) 2625.
- [9] B. Winter, M. Faubel, *Chem. Rev.* 106 (2006) 1176.
- [10] J. Jortner, *Ber. Bunsenges. Phys. Chem.* 75 (1971) 696.
- [11] A. Henglein, *Ber. Bunsenges. Phys. Chem.* 78 (1978) 1078.
- [12] J. Linderberg, Y. Öhrn, *Propagators in Quantum Chemistry*, John Wiley & Sons, New Jersey, 2004.
- [13] B.T. Pickup, O. Goscinski, *Mol. Phys.* 26 (1973) 1013.
- [14] L.S. Cederbaum, W. Domcke, *Adv. Chem. Phys.* 36 (1977) 205.
- [15] J.V. Ortiz, *J. Chem. Phys.* 104 (1996) 7599.
- [16] C. Buth, R. Santra, L.S. Cederbaum, *J. Chem. Phys.* 119 (2003) 7763.
- [17] P. Cabral do Couto, S.G. Estácio, B.J. Costa Cabral, *J. Chem. Phys.* 123 (2005) 054510.
- [18] D.P. Chong, O.V. Gritsenko, E.J. Baerends, *J. Chem. Phys.* 116 (2002) 1760.
- [19] S. Hamel, P. Duffy, M.E. Casida, D.R. Salahub, *J. Electron Spectrosc. Relat. Phenom.* 123 (2002) 345.
- [20] K. Coutinho, S. Canuto, *Adv. Quantum Chem.* 28 (1997) 89.
- [21] K. Coutinho, S. Canuto, *J. Chem. Phys.* 113 (2000) 9132.
- [22] C. Adamo, V. Barone, *J. Chem. Phys.* 108 (1998) 664.
- [23] D.E. Woon, T.H. Dunning Jr., *J. Chem. Phys.* 98 (1993) 1358.
- [24] P. Cabral do Couto, R.C. Guedes, B.J. Costa Cabral, J.A. Martinho Simões, *J. Chem. Phys.* 119 (2003) 7344.
- [25] M.J. Frisch et al. GAUSSIAN-03, Rev. C.02 Gaussian Inc., Pittsburgh, PA, 2003.
- [26] T.H. Dunning Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [27] M.W. Mahoney, W.L. Jorgensen, *J. Chem. Phys.* 112 (2000) 8910.
- [28] O. Dutuit, A. Tabche-Fouhaile, I. Nenner, H. Frolich, P.M. Guyon, *J. Chem. Phys.* 83 (1985) 584.
- [29] C.Y. Ng, D.J. Trevor, P.W. Tiedemann, S.T. Ceyer, P.L. Kronbusch, B.H. Mahan, Y.T. Lee, *J. Chem. Phys.* 67 (1977) 4235.
- [30] O. Björneholm, F. Federmann, S. Kakar, T. Möller, *J. Chem. Phys.* 111 (1999) 546.
- [31] H.M. Lee, S.B. Suh, P. Tarakeshwar, K.S. Kim, *J. Chem. Phys.* 122 (2005) 044309.
- [32] J. Kim, I. Becker, O. Cheshnovsky, M.A. Johnson, *Chem. Phys. Lett.* 297 (1998) 90.
- [33] T. Malaspina, K. Coutinho, S. Canuto, *J. Chem. Phys.* 117(2002) 1692.
- [34] P. Delahay, K. Von Burg, *Chem. Phys. Lett.* 83 (1981) 250.
- [35] T. Shibaguchi, H. Onuki, R. Onaka, *J. Phys. Soc. Jpn.* 42 (1977) 152.