

# Real-space pseudopotential calculations of the ground-state and excited-state properties of the water molecule

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Excitation energies, normal modes of vibration and geometries of the electronically excited states of the water molecule are calculated using time-dependent density functional theory with *ab initio* pseudopotentials and the local density approximation. We express electronic orbitals on a real-space grid with no explicit basis set; as such, no polarization functions are required. Convergence is controlled by a single parameter, the grid spacing. It is found that for the first and second excited states the time-dependent local density approximation predicts a metastable configuration, in disagreement with published results using asymptotically corrected functionals that correctly predict the photodissociation of the molecule. It is shown that applying the real space method with the asymptotically corrected local density approximation reproduces the previous results. The polarizability of the water molecule is calculated using the time dependent local density approximation as well as using the asymptotically corrected local density approximation.

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Water has historically been one of the most studied substances. It is not only fundamental to the existence of life, but it is also one of the main products of the combustion of hydrocarbon fuels [1,2]. The study of the energy levels of the water molecule has important applications in atmospheric science, astronomy, and combustion, and because of its unique characteristics it is also of intrinsic spectroscopic interest [1]. More recently, the effect of hydrogen bonding in the optical spectrum of liquid water has been investigated [3]. The investigation of electronic spectra can provide information about the geometries of the excited states and various quantities such as ionization potentials and dissociation energies [4]. Spectroscopy in the vacuum ultraviolet range is challenging because the water molecule is known to photodissociate at 5.1 eV [1]. As a result, the absorption spectrum tends to be diffuse [1,4].

Theoretically, the energy levels of the water molecule have been studied using molecular models, as well as empirical and *ab initio* potential surfaces [1]. Vertical excitations have been calculated by Andrejkovics and Nagy [5], who found poor agreement between theory and experiment for the lowest-energy excited states of the isolated molecule. In their work, excited states were studied using an ensemble theory based on uncorrelated excitations from the ground state of the molecule, as predicted within density-functional theory (DFT). Cai, Tozer, and Reimers [6] employed asymptotically corrected (TDHCTH) and hybrid (TDB3LYP) functionals in the framework of time-dependent DFT (TDDFT), obtaining excitation energies in closer agreement with corresponding experiments. In the last work, electronic states were expanded in a basis of localized functions.

Our approach is based on TDDFT, with two approximations, the local density approximation (LDA) of Ceperley

and Alder [7] and an adiabatic approximation for the exchange correlation functional [8]. Electronic wave functions are expressed directly in real space by means of a regular, cubic grid. Differential operators are evaluated using a high-order finite difference method [9] and degrees of freedom associated to core electrons are taken into account by using norm-conserving pseudopotentials as proposed by Troullier and Martins [10]. This technique, described in Refs. [11–13], has been successfully applied in the framework of time dependent LDA (TDLDA) in a variety of different systems [9,11,14–17]. Our results are compared with experiment and with other computational approaches such as TDB3LYP and TDHCTH.

Within TDLDA, the response of the system is solved for within a frequency domain as opposed to a real time representation [18]. The excitation energies  $\Omega_n$  may be obtained from a solution of the Casida equation [8,11],

$$\mathbf{Q}\mathbf{F}_n = \Omega_n^2 \mathbf{F}_n. \quad (1)$$

The matrix  $\mathbf{Q}$  is given by

$$Q_{ij\sigma,kl\tau} = \delta_{i,k}\delta_{j,l}\delta_{\sigma,\tau}\hbar^2\omega_{kl\tau}^2 + 2\hbar\sqrt{\lambda_{ij\sigma}\omega_{ij\sigma}}K_{ij\sigma,kl\tau}\sqrt{\lambda_{kl\tau}\omega_{kl\tau}}, \quad (2)$$

where  $\lambda_{kl\tau} = n_{l\tau} - n_{k\tau}$  is the difference between the occupation numbers, and  $\hbar\omega_{kl\tau} = \epsilon_{k\tau} - \epsilon_{l\tau}$  is the difference between the eigenvalues of the single-particle states. The oscillator strengths  $f_n$ , are then given by [11]

$$f_n = \frac{2m}{3\hbar^2} \sum_{\hat{\beta}=\{x,y,z\}} \delta_{i,k}\delta_{j,l}\delta_{\sigma,\tau} |\hat{\beta}\sqrt{\lambda_{kl\tau}\omega_{kl\tau}}\mathbf{F}_n|^2. \quad (3)$$

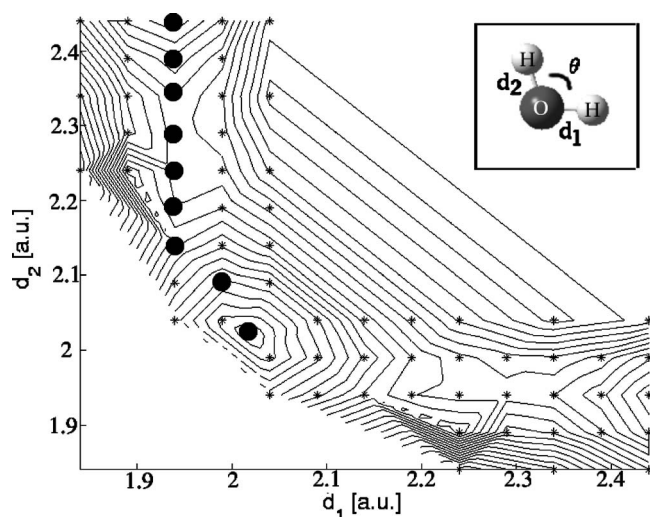


FIG. 1. TDLDA energy contours drawn with a separation of 0.005 eV. The small crosses represent all configurations that were calculated, while the large dots show the configurations used in the energy profile plots in Fig. 4.  $d_1$  and  $d_2$  refer to the two bond lengths shown in the inset, in atomic units. The equilibrium bond length is 2.02 a.u. and the bond angle is fixed at  $104.2^\circ$ .

The Casida formalism is easier to implement on parallel computer platforms, and has a smaller prefactor compared to real time methods. In addition, it can be used to study either a few selected excitations or all excitations in the visible and soft ultraviolet ranges. On the other hand, real-time methods can be equally efficient in terms of memory usage and scaling [18].

There are several advantages to the present method. The calculations are done in a real-space grid in a spherical boundary. Unlike traditional quantum chemistry methods, which employ a basis function, real space methods do not use an explicit basis. Convergence can be controlled by a single parameter, the grid spacing. This situation is similar to plane-wave methods where the basis is controlled by a single parameter, the maximum reciprocal lattice vector; and it is in contrast to methods using a basis set where the ground-state basis needs to be augmented in the presence of a perturbing electric field by polarization functions. As such, real-space methods are straightforward to implement and often require much less computational load.

Several interesting properties of the ground state and excited states of the water molecule can be calculated using the TDLDA framework described above. The first of these properties is the excitation energies, from which the corresponding vibrational levels and the relaxed geometry of each state can be calculated. Convergence within 0.1 eV for the energy of the ground state and of the excited states was achieved with a boundary sphere radius of 12 a.u. (where 1 a.u. = 0.529 Å), a grid spacing of 0.25 a.u. and 100 empty states.

There are three internal coordinates in the water molecule, two bond lengths,  $d_1$  and  $d_2$ , and one angle,  $\theta$  (shown as an inset in Fig. 1). Therefore, there are three normal modes of vibration, symmetric stretch, asymmetric stretch, and bending. The frequencies associated with the normal modes of

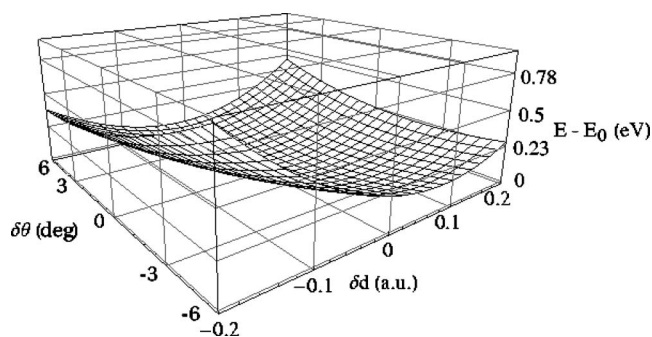


FIG. 2. Ground-state energy as a function of displacement from equilibrium of one bond length and angle (second bond length held constant).

vibration can be obtained by finding a nontrivial solution to the Lagrangian equations of the system, where the potential and kinetic energy tensors are expressed as a function of the normal coordinates. The values of the force constants associated with the potential energy tensor of the water molecule can be found by changing the geometry of the molecule in order to obtain a fit for the energy as a function of the coordinates, and then taking the appropriate second derivatives. The relaxed geometry is simply the minimum of the energy surface, shown in Fig. 2 as a function of the displacement of one of the bond lengths and of the angle.

Calculations were made for approximately 40 different geometries. The calculated values for the geometrical configurations of the ground state and excited states show excellent agreement with experiment, as can be seen in Table I. The geometrical parameters (bond length and angle) are within 2% of the experimental values reported by Herzberg [4].

The ground-state and excited-state energies as a function of the displacement of one of the bond lengths,  $\delta d$  (with the angle set at the equilibrium ground state value,  $\theta = 104.2^\circ$ ), are shown in Fig. 3. We find that the calculated optical excitation energies differ from experimental values by 10%–15%. Within the TDLDA approximation, the energy surfaces for the first four excited states show minima that give rise to real vibrational frequencies. The agreement for vibrational frequencies ranges from 20% to 30%. The difference between the calculated value and experiment is greater for the higher states.

To put our results in context, and assess the reliability of our method, we compare our results for the excited state properties of the water molecule with those of Cai, Tozer, and Reimers [6] in Table I. With the exception of state  $\tilde{B}(^1A_1)$ , we found a tendency towards underestimation of the relaxed excitation energy in TDLDA compared to TDHCTH. This can be understood as an effect of the exponential decay of the local-density exchange-correlation potential in the LDA. As a result, occupied electronic orbitals of the molecule are pushed to higher energies, reducing the energy gap between occupied and unoccupied orbitals and hence excitation energies. Asymptotically corrected functionals like TDHCTH are expected to give a more reliable description of excitations in the system. Measured excitation energies typically fall in between the values predicted by TDLDA and TDHCTH.

TABLE I. Calculated and experimental values of relaxed excitation energies ( $T_e$ ), normal modes of vibration  $\nu$  and geometries (bond length,  $d$ , and angle,  $\theta$ ) of the ground state and excited states of the water molecule.

Method	$T_e$ (eV)	$\nu_1$ (cm $^{-1}$ )	$\nu_2$ (cm $^{-1}$ )	$\nu_3$ (cm $^{-1}$ )	$d$ (a.u.)	$\theta$ (deg)	
State $\tilde{X}^1A_1$							
Experiment [4]		3657.0	3755.7	1594.7	1.81	104.5	
This work (LDA)		3811	3667	1606	1.84	104.2	
This work (ACLDA)		3772	3787	1639	1.86	103.9	
Cai <i>et al.</i> [6]							
B3LYP		3790	3893	1628	1.82	104.5	
HCTH		3776	3888	1628	1.82	104.2	
State $\tilde{A}^1B_1$							
Experiment [4]	6.67	(continuous absorption, broad max. at 1655 Å)					
This work (TDLDA)	6.2	3407	3035	893	2.02	105.6	
This work (TDACLDA)	6.8	2853	2242 <i>i</i>				
Cai <i>et al.</i> [6]							
TD-B3LYP	6.71	2402	1161 <i>i</i>	1187	1.96	105.7	
TD HCTH	7.43	2427	359 <i>i</i>	1033	1.97	103.6	
State $\tilde{B}^1A_1$							
Experiment [4]	8.79			800		180	
This work (TDLDA)	8.3	3439	3443	872	1.96	180.5	
This work (TDACLDA)	8.5	1063	4105 <i>i</i>				
Cai <i>et al.</i> [6]							
TD-B3LYP	7.06	1817	2377 <i>i</i>	1582	2.26	180	
TD HCTH	7.27	1434	2844 <i>i</i>	2077	2.40	180	
State $\tilde{C}^1B_1$							
Experiment [4]	10.0	3170	3224	1422	1.91	106.9	
This work (TDLDA)	8.5	3692	3695	1838	1.93	108.9	
This work (TDACLDA)	8.9	3277	2930	1850	1.97		
Cai <i>et al.</i> [6]							
TD-B3LYP	8.51	3568	3636	1509	1.862	108.4	
TD HCTH	9.99	3713	3801	1568	1.83	102.7	
State $\tilde{D}^1A_1$							
Expt. [4,20]	10.17	3268	3335	1636	1.94	113.0	
This work (TDLDA)	8.6	3657	3590	2302	1.97	112.6	
This work (TDACLDA)	10.1	3518	3387	1242	1.90	108.8	
Cai <i>et al.</i> [6]							
TD-B3LYP	8.59	4018	3609	3213	1.86	114.9	
TD HCTH	10.22	3742	3865	1836	1.82	105.9	

When available, measured vibrational frequencies of excited states are found to be similar to the TDLDA prediction. Intriguingly, TDLDA does not predict photodissociation in the first spin-singlet excitation,  $\tilde{X}^1A_1$ . Instead, it predicts a metastable configuration with bond length 2.02 a.u. and bond angle 105.6°. Functionals TDB3LYP and TDHCTH [6] predict instead the existence of a saddle-point configuration with real frequencies for the symmetric stretch and bond bending modes. According to these functionals, the molecule is unstable with respect to distortions along the asymmetric stretch mode. Strong distortions along this mode result in

dissociation following the chemical reaction  $H_2O \rightarrow OH^- + H^+$ .

The question arises whether the discrepancy is due to an inherent characteristic of the real-space method or a result of the fact that the TDLDA functional is not asymptotically correct, unlike the TDB3LYP and TDHCTH functionals. In order to answer this question, calculations on several geometric configurations were done using the asymptotically corrected local density approximation (TDACLDA) proposed by Casida and Salahub [19]. These configurations, which were chosen such that they go along the barrier in the

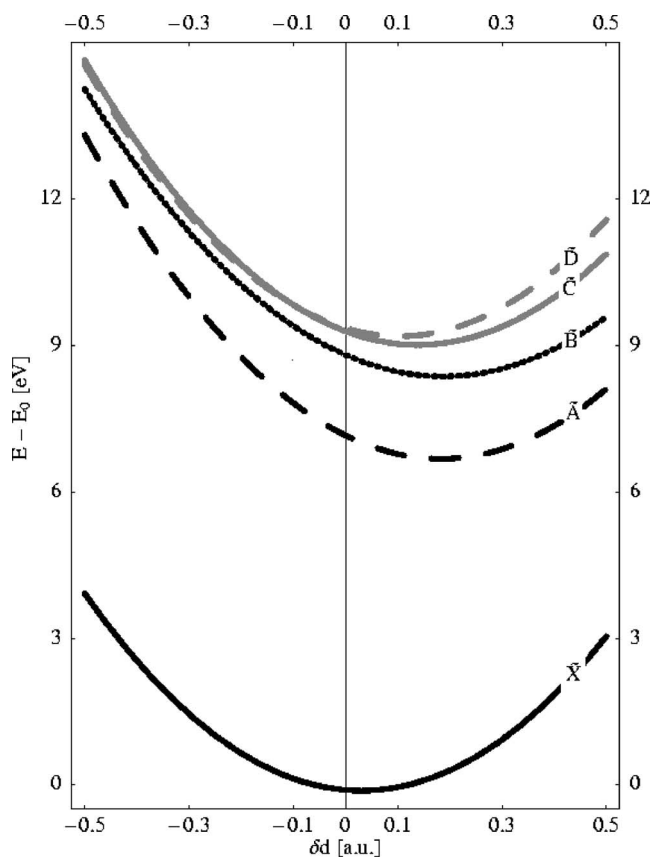


FIG. 3. Energy as a function of displacement from equilibrium of one bond length (angle set at equilibrium value for ground state).

TDLDA energy contours, are indicated in Fig. 1. Figure 4 shows the total energy (ground-state energy plus excitation energy) for these limited number of configurations. One can see clearly the existence of a low energy barrier separating the metastable configuration (as predicted by TDLDA, top panel of Fig. 4 and also in Fig. 1) and the dissociation limit. On the other hand, TDACLD predicts a monotonic energy profile with no barrier (bottom panel). State  $\tilde{B}(^1A_1)$  is also found to have a metastable configuration within TDLDA. This indicates that the metastable configuration is an artifact of TDLDA.

The vibrational frequencies obtained using the TDACLD functional are labeled in Table I as “This work (TDACLD).” The asymmetric vibrational mode for the first and second excited states is imaginary as expected from the previous discussion, where we showed that the energy profile for TDACLD does not present an energy barrier. When we compare the TDACLD vibrational frequencies to previous calculations, namely TDB3LYP and TDHCTH, we see that although the agreement is quite reasonable for the symmetric mode ( $\nu_1$ ), there is still a large discrepancy between all calculations for the asymmetric mode ( $\nu_2$ ). Calculation of the bending vibrational mode and geometry of the first and second excited states requires a very precise knowledge of the energy surface due to the presence of the saddle point.

The static polarizability and absorption cross section of the water molecule are two excited state properties of considerable scientific interest. The polarizability is fundamental

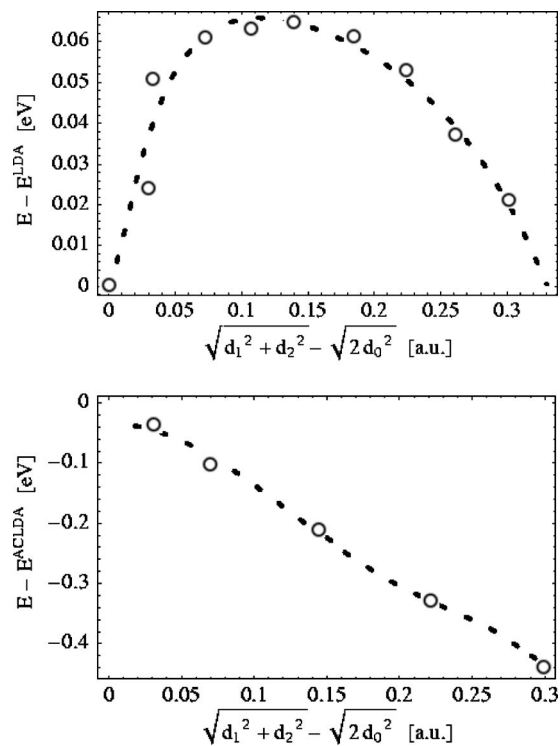


FIG. 4. Total energy of the water molecule in state  $\tilde{A}(^1B_1)$ , calculated within TDLDA (top panel) and TDACLD (bottom panel), as a function of bond lengths. The energy is referenced to the equilibrium configuration energy for the first excited state in each approximation ( $E^{\text{LDA}} = -460.08$  eV,  $E^{\text{ACLD}} = -459.26$  eV). Location of the configurations is indicated in Fig. 1. The equilibrium bond length, labeled  $d_0$ , is 2.02 a.u.

for the understanding of interactions between water molecules and also between water and biomolecules [22], while the absorption cross section is important in the studies of photodissociation of water vapor by solar radiation [25].

In this work, the polarizability was obtained using both the LDA and ACLDA functionals. In LDA, the polarizability was calculated in two different ways. The first was using the sum-over-states formula of TDLDA given by the equation below,

$$\alpha_{\text{static}} = \frac{\hbar^2 e^2}{m} \sum_n \frac{f_n}{\Omega_n^2}, \quad (4)$$

where  $\Omega_n$  and  $f_n$  are the excitation energies and oscillator strengths as defined in Eqs. (1) and (3). In this case a radius of 12 a.u. was used, with a grid spacing of 0.33 a.u. and 300 empty states. The second way of calculating the polarizability, which was also used in the ACLDA calculations, is by the finite field (FF) method [26]. The results (labeled TDLDA, FFLDA and FFACLD) are shown, along with other groups' results for comparison, in Table II. TDLDA, FFLDA, and FFACLD results are in reasonable agreement with the known experimental value, the first two overestimating the value by about 10% while the second underestimates it within 3%. Indeed, the FFACLD calculation for

TABLE II. Calculated and experimental values of the polarizability of the water molecule.

Method	$\alpha$ (a.u.)
Experiment [21]	9.8
This work (TDLDA)	10.67
This work (FFLDA)	10.95
This work (FFACLDA)	9.55
Hartree-Fock [22]	6.34
B3LYP [22]	7.21
MP2/aug-cc-p VDZ [23]	9.29
Static TDDFT [24]	9.15

polarizability gives the most accurate result of the methods shown in Table II.

Within the TDLDA framework, once the oscillator strengths  $f_n$  and excitation energies  $\Omega_n$  are known, the absorption cross section may be obtained using Eq. (5),

$$\sigma(\omega) = \frac{e^2 \pi^2 \hbar}{mc} \sum_n f_n \delta(\hbar\omega - \Omega_n). \quad (5)$$

The resulting spectrum was broadened using a Gaussian of width 0.4 eV, which is of the order of the vibrational energy of the molecule ( $\sim 3000 \text{ cm}^{-1}$ ). The broadening was done in order to simulate the finite temperature and resolution of the experimental data. The TDLDA absorption cross section is shown in Fig. 5 along with an experimental measurement at a temperature of 295 K by Yoshino *et al.* [25]. The shape and amplitude of the TDLDA spectrum are in very good agreement with the experimental spectrum. Examination of Fig. 5 shows that the TDLDA spectrum is shifted toward higher wavelengths (lower energies) which is analogous to the systematic TDLDA underestimation of excitation energies, as was seen in Table I.

In conclusion, ground state and excited state geometries, energies, and vibrational frequencies as well as the polarizability and absorption cross section of the water molecule were calculated within the TDLDA framework using a real-space pseudopotential method. A significant difference in the results for the vibrational modes of the first and second excited states was found when comparing TDLDA to previously presented calculations that used asymptotically cor-

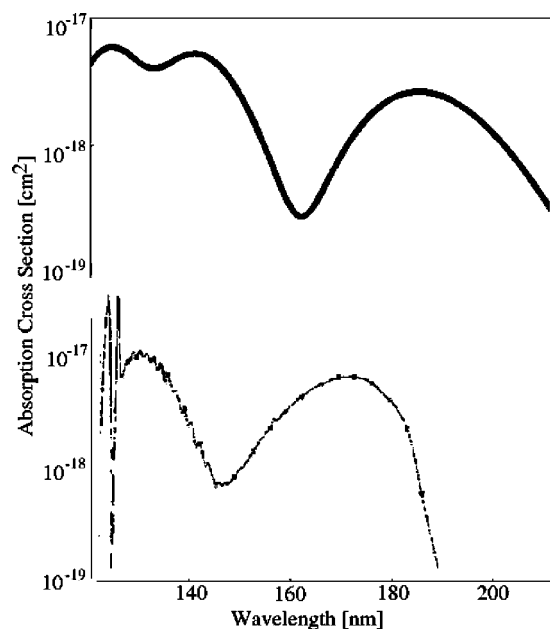


FIG. 5. Absorption cross section of water as calculated with TDLDA (top) and measured (bottom) [25].

rected functionals. TDLDA predicts a small energy barrier for the dissociation of the first and second excited states which results in a real vibrational frequency, while TDB3LYP and TDHCTH correctly predict the dissociation of the water molecule. This discrepancy was studied using an asymptotically corrected functional in the real-space pseudopotential method and it was shown that the choice of functional leads to the different predictions. In addition, the polarizability of the water molecule was calculated using the finite field method both for LDA and ACLDA.

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