

**Sequential classical-quantum description of the absorption spectrum of the hydrated electron**Valdemir Ludwig,<sup>1</sup> Kaline Coutinho,<sup>2</sup> and Sylvio Canuto<sup>1,\*</sup><sup>1</sup>*Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970, São Paulo, SP Brazil*<sup>2</sup>*Universidade de Mogi das Cruzes, CP 411, 08701-970, Mogi das Cruzes, SP, Brazil*

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A localized state of the electron in water is assumed to study the absorption spectrum of the hydrated electron. A classical Monte Carlo statistical mechanics simulation is used to generate the structure of water in the field of the hydrated electron. These structures are used in quantum mechanical calculations of the absorption spectrum using time-dependent density-functional theory. The statistically converged spectral distribution is in good agreement with experiment. The value obtained here for the maximum of the absorption profile is 1.70 eV with a half-width of 0.90 eV, in comparison with the corresponding experimental values of 1.725 and 0.84 eV.

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**I. INTRODUCTION**

An excess electron in the aqueous environment leads to a transient species that has attracted considerable interest.<sup>1</sup> The characteristic feature of this hydrated electron is its strong and broad absorption spectrum, first recorded four decades ago<sup>2</sup> and confirmed several times later.<sup>3</sup> It shows an intense and broad peak located in the visible region with a maximum at  $\lambda=720$  nm (1.725 eV). The theoretical description of the absorption spectrum of an excess electron in a solvent has attracted wide interest.<sup>4–20</sup> There are some successful models based on the path integral formulation of quantum mechanics.<sup>21</sup> Noteworthy is the pioneering work of Schnitker *et al.*<sup>9</sup> that gave essentially all the qualitative features of the structure and optical absorption spectrum, but resulted in too high excitation energy compared to experiment. Similar treatments based on the path integral formulation with the electron-water interaction based on a parametrized pseudopotential have obtained partial but conceptually important results.<sup>7,9</sup> More recently, Boreo and co-workers<sup>20</sup> have presented a first-principles molecular dynamics study of the hydrated electron both in normal and supercritical water. This simulation was based on the density-functional theory (DFT) within the Becke-Lee-Yang-Parr (BLYP) exchange correlation<sup>22</sup> on a system composed of 32 water molecules. The resulting spectrum (with a calculated peak at 1.74 eV) was in good agreement with experiment.

An accurate theoretical treatment of the solvated electron can be obtained by quantum simulation. As a description of a liquid requires statistical mechanics, a quantum molecular dynamics is the natural method of choice. Because of the large computational effort involved, (i) a relatively small number of molecules is normally used to represent the liquid, (ii) the simulation is relatively small, and (iii) statistical convergence cannot always be assured. This makes it more difficult to study larger systems of chemical interest, such as ethylene glycol.<sup>23</sup> It would thus be of interest to alleviate the computational demand. In this work we show an alternative and promising method based on a *classical* description of the structure of the hydrated electron. The conformations of the water molecules are obtained using a classical statistical me-

chanics simulation. This is parallel but dissimilar to the original ideas of Barker<sup>24</sup> and Chandler and Wolynes.<sup>25</sup> They have considered a discretization of the path integral formulation of quantum mechanics and discussed the isomorphism between quantum theory and classical statistical mechanics.<sup>26</sup> Here we explore the possibility of treating the hydrated electron by means of classical statistical mechanics. Monte Carlo simulation is made to generate the structure of the liquid, and first-principles quantum mechanical calculations are performed on sampled structures to obtain the absorption spectral profile of the hydrated electron.

**II. METHODS**

We assume the existence of a localized, transient state and use classical Monte Carlo (MC) simulation to generate the liquid conformations that are necessary for the ergodic representation of the hydrated electron. Next, we use these structures to perform the quantum mechanics calculations of the optical spectrum. We first use MC simulation to generate an ensemble of configurations and perform the quantum mechanical (QM) calculations subsequently. These are made at the time-dependent DFT (TD-DFT) level<sup>27</sup> using the three-parameter Becke-Lee-Yang and Parr (B3LYP) exchange correlation functional with a localized Gaussian-type basis function 6-31++G( $d,p$ ), which includes both diffuse and polarization functions. Performing the classical simulations prior to the QM has the advantage that an analysis of the statistical correlation between successive MC configurations can be made to ensure statistical convergence.

The configurations of the excess electron in water are obtained from the isothermal-isobaric  $N$ - $P$ - $T$  MC simulation. It is expected that the absorption profile will depend on the structural arrangement of the water molecules around the trapped electron. The charge density distribution of the electron is represented by a charge  $q=-1$  and the two Lennard-Jones parameters ( $\epsilon=0.08$  kcal/mol and  $\sigma=4.04$  Å) were obtained to reproduce the experimental distance<sup>28–30</sup> between the center of the charge of the excess electron and the water molecules in the first hydration shell. These parameters, in addition, describe well the number of water molecules in the

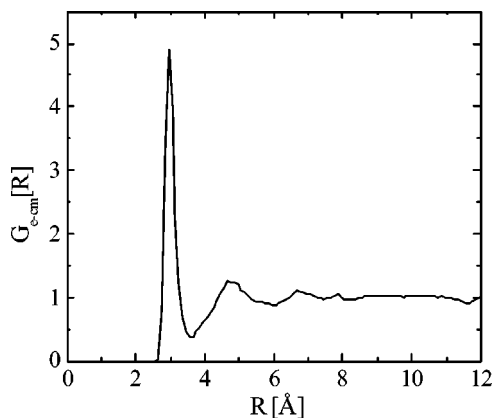


FIG. 1. Classical pairwise radial distribution function between the center of the electron charge distribution and the center of mass of the water molecules.

first hydration shell. The simulations are made in a cubic box with 500 water molecules represented by the simple-point-charge (SPC) potential<sup>31</sup> at the temperature of 298 K. After thermalization, the MC simulation was performed with a total of  $2 \times 10^7$  steps using DICE.<sup>32</sup>

### III. RESULTS AND DISCUSSION

Figure 1 shows the pairwise radial distribution function between the center of the electron distribution and the center of mass of the water molecules obtained from the MC simulation. There is a clear and sharp peak starting at 2.6 Å and ending at 3.6 Å with a pronounced maximum at 3.0 Å. This corresponds to the hydrogen-bond-type shell where the hydrogen atom of the OH bond of water points to the negative charge, as indeed inferred experimentally<sup>28</sup> and discussed before.<sup>29</sup> This orientation of the water molecules corroborates results obtained with electron spin resonance.<sup>30</sup> This is also the picture that emerges from the work of Miura and Hirata<sup>7</sup> and Schnitker *et al.*<sup>9</sup> using QM path integral and emphasized by the work of Kim *et al.*<sup>8</sup> The integration of the first peak in the radial distribution gives the coordination of water molecules around the hydrated electron. Our calculations give the average number of 6.9 water molecules. The time-of-flight spectrum of water anions<sup>33</sup> has shown considerable intensity for species with 6 and 7 water molecules. If the liquid situation should reflect an average of possible structures, it is conceivable that the average number should be between 6 and 7. Our average of 6.9 is in line with this experimental result. In the liquid case the number of water molecules in the first hydration shell is not known. The liquid result obtained here reflects closely the cluster abundance. Opposite to the liquid situation considered here, where the statistical treatment includes several structures at a given temperature, in cluster studies the geometry is fixed by a minimum-energy optimized structure. There are several cluster studies.<sup>33–36</sup> Boero *et al.*<sup>20</sup> have defined an anisotropic parameter to characterize the shape of the hydration shell,  $W = 1 - (J_1 + J_2) / 2J_3$ , where  $J_1 \leq J_2 \leq J_3$  are the moments of inertia. Our calculated average value for the first solvation shell is  $W = 0.2$ , indicating the extent of the asymmetry. In

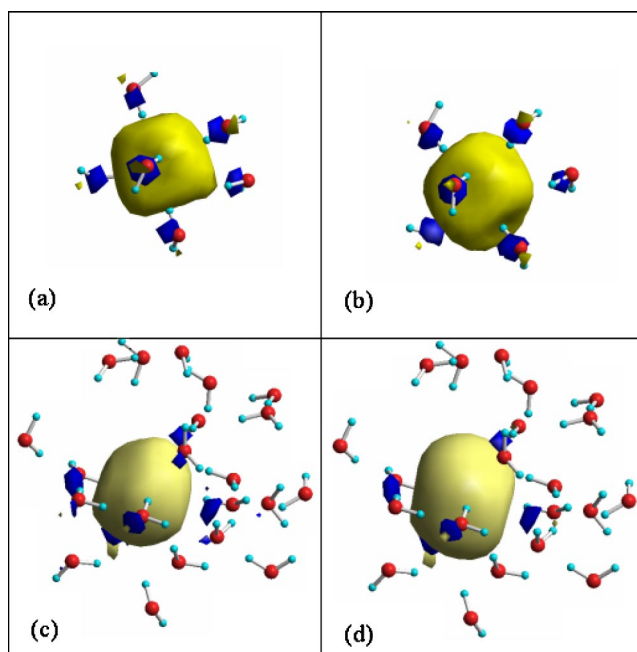


FIG. 2. Illustration of the molecular orbital of the excess electron. (a) and (b) are Kohn-Sham and Hartree-Fock orbitals using the same configuration of the first hydration shell, respectively. (c) and (d) are the same for the second hydration shell.

agreement with Boero *et al.*<sup>20</sup> we also find an average elliptical cavity for the electron. Figure 1 also identifies a second hydration shell ending at 6.0 Å. Integration of the radial distribution function up to 6.0 Å gives coordination of 23 water molecules up to the second hydration shell. The structure of the first solvation shell is one important characterization of the transient state of the hydrated electron. This first hydration shell is expected to dominate the theoretical description of the absorption spectrum,<sup>20</sup> and it will be considered first. Next we will consider the second hydration shell. Our TD-DFT calculations will now be performed on the MC configurations composed of 7 water molecules and an extra electron (71 electrons). The wave function is antisymmetric with respect to all 71 electrons. We are now taking into account the indistinguishability between the excess and any of the water electrons. Before running the QM calculations it is important to ensure statistical convergence.<sup>37–39</sup> Therefore we calculate the interval of statistical correlation using the autocorrelation function of the energy.<sup>40–42</sup> For the simulations presented here, we obtain that configurations separated by  $3 \times 10^5$  MC steps are statistically uncorrelated. Then, the  $2 \times 10^7$  successive MC configurations yield 65 uncorrelated configurations that are sampled for use in TD-DFT calculations of the optical absorption spectrum. As we shall see this is enough to give accurate and statistically converged results. Figure 2 shows for one of the selected configurations the quantum mechanical density of the molecular orbital (MO) of the excess electron. MO's have a clearer physical meaning in the Hartree-Fock model, and Fig. 2 shows the resemblance of the Hartree-Fock and Kohn-Sham orbitals that represent the excess electron. The outermost occupied MO is very diffuse, and in spite of the nonspherical structure it is commonly referred to as an *s*-type orbital. Similarly, the three lowest

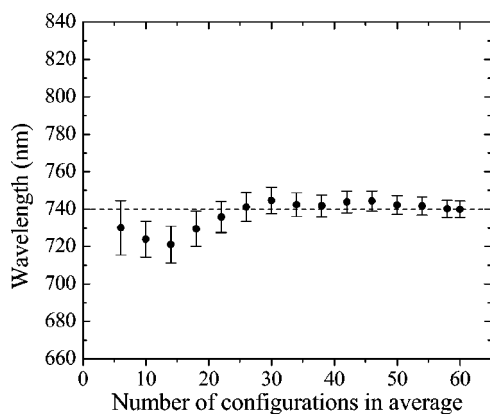


FIG. 3. Statistical convergence of the average transition wave number for the first hydration shell.

unoccupied MO's have approximate  $p$ -type symmetry and the excitation process has been termed an  $s \rightarrow p$  like transition. In fact this is only an approximate,<sup>20</sup> although convenient, picture and a true spherical symmetry is not obtained. Using these three  $s \rightarrow p$  type transitions for the 65 configurations generated in the MC classical simulation we obtained the average transition energy as  $\langle \lambda \rangle = 740 \pm 20$  nm. Figure 3 demonstrates the statistical convergence by showing the average transition energy. As can be seen convergent results are obtained already for 35 TD-DFT calculations. This emphasizes the importance of the analysis of the statistical correlation and also the efficiency of the classical MC simulation in generating realistic configurations for subsequent QM calculations. It is now of importance to consider the second hydration shell, composed of 23 water molecules. Similar TD-DFT calculations were performed on statistically uncorrelated structures composed of all water molecules up to the second shell ( $R \leq 6.0$  Å). The wave function is now antisymmetric for the entire system composed of 231 electrons explicitly considered. As a compromise the polarization function in the H atom has been excluded, without affecting the final accuracy (see below). A better comparison with the experimental result can be made obtaining the profile of the optical absorption spectrum in this spectral region. From a theoretical point of view it is imperative that converged statistical distribution be used. Figure 4 shows the converged statistical data using the histogram of calculated values. The theoretical line shape is a convolution of the individual Lorentzian line shapes. The calculated transitions give a statistical distribution that is asymmetric and the experimental result is associated with the maximum of this distribution. The theoretical value at the maximum (the most probable

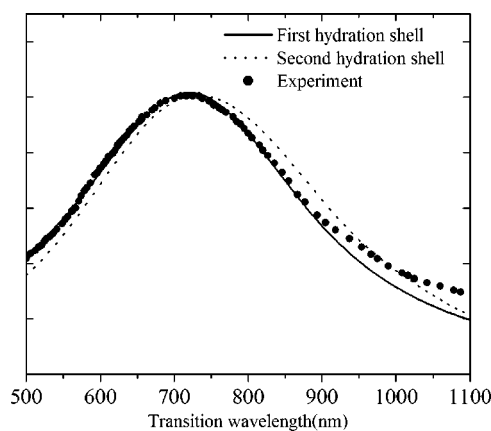


FIG. 4. Comparison between the theoretical and experimental (Ref. 3) profiles of the optical absorption spectrum.

value) is  $\lambda_m = 721$  nm, for the first hydration shell, and 729 nm if we use all water molecules up to the second hydration shell, in good agreement with experiment<sup>1-3</sup> (720 nm). It is of interest to note that the inclusion of only the water molecules in the first hydration shell already leads to a good description of the absorption spectrum for the entire range of spectral values. The calculated width at half maximum is calculated as 0.90 eV (555–940 nm, in Fig. 4), again in good agreement with the experimental result of 0.84 eV. Table I compares our results with previous theoretical and experimental values, showing the adequacy of the present treatment.

#### IV. CONCLUSIONS

The present study shows that classical statistical mechanics combined with an adequate quantum mechanical treatment of the excitation spectrum leads to all the essential aspects of the absorption spectrum of the hydrated electron. The structure of the water molecules around the localized state of the excess electron is obtained from classical Monte Carlo simulation and leads to a good representation of the configuration spanned by the transient state. Using these structures quantum mechanical calculations of the excitation energies are performed on statistically uncorrelated configurations, leading to results for the spectral profile in good agreement with experiment. The use of only the first hydration shell already leads to a good description. The classical

TABLE I. Calculated transition energy and half-width (in eV) for the hydrated electron.

	Ref. 43	Ref. 9	Ref. 7	Ref. 20	Present	Expt. (Ref. 3)	
Transition	2.1	2.4	2.6	1.74	1.72 <sup>a</sup>	1.70 <sup>c</sup>	1.725
Width	-	1.1	-	0.95	0.89	0.89	0.84

<sup>a</sup>TD-DFT/6-31++G( $d,p$ ) on the first hydration shell (7 water molecules).

<sup>b</sup>TD-DFT/6-31++G( $d$ ) on the first hydration shell (7 water molecules).

<sup>c</sup>TD-DFT/6-31++G( $d$ ) up to the second hydration shell (23 water molecules).

potential is used here only after assuming a localized transient state. Changes in the potential and in the quantum mechanical model used lead to small changes in the calculated absorption transition. However, the importance of the statistics can be probed by the calculated line shape. The statistically converged result obtained here for the maximum value of the absorption profile is 1.70 eV and the half-width

value is 0.90 eV, in comparison with the corresponding experimental values of 1.725 and 0.84 eV.

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