

On the effect of solute-solvent Pauli repulsion on $n \rightarrow \pi^*$ transition for acrolein in water solution

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Abstract

In this work, we present a method to compute the Pauli repulsion contribution to the solute-solvent interaction that exploits solute electronic configurations sampled by Quantum Monte Carlo simulations. Starting from the inspiring model of Amovilli and Mennucci, the discreteness of the solvent is recovered by the definition of molecular domains and the concept of probe molecule. The method can be calibrated on the solute ground state but it offers the advantage of being able to be applied also to electronic excited states. We show the results for the formaldehyde-water intermolecular pair, here used for the calibration, and two clusters containing acrolein surrounded by 11 and 19 water molecules simulating the solvation shell. In these systems, hydrogen bonds are formed between the solute and the water molecules and we found that, in such case, the Pauli repulsion contribution gives a red shift in the $n \rightarrow \pi^*$ vertical transition energy.

Keywords: Solvatochromic effect. Pauli repulsion. Solvation. Quantum Monte Carlo.

1 Introduction and general theory

The nonelectrostatic interactions with the solvent could play some role in tuning the electronic excitation of molecular solutes [1]. The effect of the environment on a molecular system is typically investigated through the so called quantum mechanics/molecular mechanics (QM/MM) [2, 3, 4] and quantum mechanics/continuum models [5, 6]. In both methods, the environment is treated classically, in the first by an atomistic description and in the second by means of a structureless dielectric continuum. Several extensions to non classical treatment of the solvent have been considered in the last two decades [7, 8, 9, 10, 11, 12, 13, 14]. The most important non-classical interactions are the dispersion and the Pauli repulsion terms [15]. In particular, within the continuum models, Amovilli and Mennucci [8] derived an expression for these two contributions to the free energy of solvation by starting from the theory of intermolecular forces [15].

In this work, we revise Amovilli and Mennucci approach [8] with the aim of being able to exploit all the features of the quantum Monte Carlo (QMC) method for the calculation of the Pauli repulsion contribution. In particular, we are interested to extend our approach to solutes in an excited state. Here, we follow the same route that we have already designed for the dispersion contribution in previous works [16, 17]. We present a general method to compute Pauli repulsion energy by using electronic sampled configurations generated by QMC. In this step, one of the two interacting systems is modeled while the other is treated at the QMC level. This latter system can be in an excited state. In this form, the theory can be applied to the study of a solvated molecule with the solvent treated as a discrete medium.

Pauli repulsion is determined by the superposition of the electronic clouds of the two interacting systems. For this reason, it is essentially a contact term (short range). In Amovilli and Mennucci method [8], the relevant contribution to the free energy of solvation is proportional to the fraction of electrons of the solute that is found in the solvent domain and to the number of valence electrons of the solvent itself. In this work, we are interested to recover the structure of the solvent. Therefore, we redefine the Pauli repulsion between two systems A and B in the following way

$$E_{rep}(\mathbf{R}_{AB}) = \sum_j^{\text{atoms of B}} K_j(B) q_A(\mathcal{D}_{B_j}|\mathbf{R}_{AB}) \quad (1)$$

where \mathbf{R}_{AB} is the set of coordinates defining the interacting complex, q_A is the fractional number of electrons of A found in the domain \mathcal{D} of atom j of system B and $K_j(B)$ is a parametric constant typical of this atom j of B. By means of a QMC calculation, the charge q_A is easily computed from sampled electron configurations. In Figure 1, we show a schematic representation of the present model. In details, A is the system of interest, namely the solute, and B belongs to the environment. Here, B works as a probe and it counts the fraction of electrons in its domain.

In this work, as a preliminary test of the method, we study the $n \rightarrow \pi^*$ transition of formaldehyde interacting with water to parameterize the model and we apply this theory to the same transition of acrolein solvated by water. We present results for two clusters containing, respectively, 11 and 19 water molecules.

2 Quantum Monte Carlo results

As a test study, we consider acrolein solvated by water in which hydrogen bonds should play an important role in the solvatochromic shift contribution due to Pauli repulsion. In the ground state, the acrolein molecule is able to form hydrogen bonds with some water molecules of the first solvation shell by means of the carbonyl group. For this reason, the Pauli repulsion is a significant contribution to the interaction energy due to the short distances between water and acrolein. In the vertical $n \rightarrow \pi^*$ electronic transition, a fraction of the electronic charge involved in such hydrogen bonds is moved to the π^* orbital spatial domain, reducing the Pauli repulsion with the solvent for the excited state of acrolein. Thus, we expect a red shift contribution due to Pauli repulsion for this particular case. For the purpose of this work, we performed calculation on clusters of acrolein surrounded by 11 and 19 water molecules. The geometries of the two clusters have been taken from the work of Guareschi et al [18].

In order to generate a sufficiently high number of electronic configurations, we performed a standard variational QMC calculation on formaldehyde and acrolein. For the ground and excited states of acrolein we follow exactly the same recipe used in our previous works [18, 19, 20]. The same procedure has been applied to formaldehyde in the ground state geometry [21]. For the QMC calculations we used the CHAMP code [22].

In these calculations, the water molecule is treated as the probe. Ac-

cording to equation (1), we have to define the atomic radii of H and O of water and the relevant constants K_j . To this end, we fit the Pauli repulsion, computed by means of Morokuma decomposition[23], of formaldehyde water intermolecular complex at different geometries. We considered the planar geometry of Figure 2 and we moved the water molecule along a vertical axis parallel to the carbonyl of formaldehyde. Calculations were performed with the GAMESS package [24] at RHF/cc-pvTZ level. Figure 3 shows the behaviour of Pauli repulsion as a function of the intermolecular relative coordinate. The best fit, in the region of interest, namely near the minimal energy geometry, provides for the radii of H and O, respectively, the values of $2.6 a_0$ and $3.4 a_0$ with $K_H = 0.05$ a.u. and $K_O = 0.09$ a.u. With such values of atomic radii, the fraction of formaldehyde electrons in the water domain, calculated at QMC level for both ground and excited $n \rightarrow \pi^*$ state, is displayed in Figure 4. For sake of completeness, we have also computed the isolated formaldehyde $n \rightarrow \pi^*$ transition energy at diffusion Monte Carlo (DMC) level obtaining the value of 4.21 eV.

From equation (1), the solvatochromic shift due to Pauli repulsion in water solution takes the form

$$\Delta\Delta E_{rep} = 0.05 \Delta q_{inH} + 0.09 \Delta q_{inO} \quad (2)$$

where atomic units are used for charges and energies. By way of example, in Figure 5 we show this contribution as a function of the water displacement for a formaldehyde-water pair. In order to speak of solvatochromic shift one has to consider a real situation, in which a single molecule of solute is surrounded at least by a cluster of solvent molecules simulating the solvation shell. However, the example given in Figure 5 is important because it shows the magnitude of such shift due to a single solvent molecule. Here we find an interval between -0.07 and 0 eV which should be compared with 4.21 eV. The shift is not negligible and is negative, as expected because of the hydrogen bond.

As test example, we have chosen acrolein in water solution. To this end we have worked on two clusters with 11 and 19 solvent molecules, respectively, which were taken from Guareschi et al [18]. These two clusters simulate a solvation shell and are shown in Figures 6 and 7.

From QMC simulations, we obtained the electronic configurations of acrolein in ground and $n \rightarrow \pi^*$ excited states. In Table 1, we show the resulting electronic charges in the atomic solvent domains together with the

System	ground state		excited state		Δq_{inH}	Δq_{inO}
	q_{inH}	q_{inO}	q_{inH}	q_{inO}		
acrolein (11 w)	1.0886	0.2747	0.9649	0.2677	-0.1237	-0.0071
acrolein (19 w)	1.1669	0.4378	1.0495	0.4403	-0.1174	0.0025

Table 1: Electronic charge (atomic units) for ground and $n \rightarrow \pi^*$ excited state of acrolein in water volume domain for the two clusters with 11 and 19 water molecules considered in this work.

variation along the vertical excitation to be used in equation (2) to find the relevant solvatochromic shift due to Pauli repulsion. The shift is shown in Table 2 and compared in the same Table with the vertical transition energy computed for isolated acrolein at DMC level. From Table 1, it is evident that, due to the ground state geometry in which we have H-bonds, the maximum penetration of the acrolein electronic cloud occurs in the region of hydrogen atoms of the closest water molecules for both states. We notice that only few water hydrogens of the cluster are so close to the acrolein molecule and, of course, are those involved in H-bonds. The oxygen atoms instead are more homogeneously distributed around the solute in these two clusters. This explains why the fraction of electrons in the hydrogen domains is much more important in the vertical transition. The Pauli contribution to the solvatochromic shift is ranging from -0.19 to -0.15 eV, which corresponds to a non negligible red shift if compared with 3.90 eV, namely the isolated acrolein vertical transition energy. This shift is partially reduced in magnitude in going from 11 water molecules to 19 because part of the Pauli repulsion, lost in the transition, is regained by the interaction with the additional 8 water molecules of the largest cluster, these being located in the region where there are not H-bonds. We remark that the experimental solvatochromic shift for acrolein in water is 0.2 eV [25, 26]. The main reason for such a blue shift is to be attributed to the electrostatic effects that stabilize significantly the ground state due to H-bonds. It is well known that, in H-bonds, electrostatics plays a dominant role with effects greater than Pauli repulsion nevertheless, the value 0.2 eV should result from a balance of all classical and non-classical contributions. Several different theoretical calculations, based mainly on classical solute-solvent interaction terms, give a blue shift ranging from 0.10 to 0.33 eV (see, for example, [26, 27, 28, 29]).

System	ΔE (eV)	$\Delta\Delta E$ (eV)
acrolein (11 w)	3.90	-0.19
acrolein (19 w)	3.90	-0.15

Table 2: Solvatochromic effect ($\Delta\Delta E$) due to Pauli repulsion for the $n \rightarrow \pi^*$ in acrolein for the two snapshots of acrolein interacting with, respectively, 11 and 19 water molecules considered in this work.

For the future, it will be interesting to couple this simple calculation with a molecular dynamics simulation in order to have a more realistic description of solvation by averaging over thousand of snapshots.

3 Conclusions

In this work, we have attempted the calculation of the Pauli repulsion solute-solvent interaction contribution to the electronic transition energy of a molecule in a solution environment. As test case, we have chosen the $n \rightarrow \pi^*$ transition of acrolein in water. The present model extends the Amovilli and Mennucci approach [8], designed for a continuum description of the solvent, to a discrete representation of the environment. Our approach exploits the concept of solvent domain and the QMC treatment of the solute. The solvent acts as a probe measuring the fraction of solute electrons in the solvent molecular domains (made of independent atomic spheres) while the solute electronic distribution is recovered by QMC sampled configurations. The method needs a calibration that, in this work, has been performed by means of the calculation of Pauli repulsion interaction energy from Morokuma decomposition for the formaldehyde water pair. Hence, the relevant contribution to the solvatochromic shift for the $n \rightarrow \pi^*$ transition of acrolein in water has been estimated by taking two clusters of 11 and 19 water molecules with acrolein. Because Pauli repulsion is mainly a contact interaction, these clusters, made of only one solvation shell, should be sufficiently adequate to capture the relevant effect. We found a shift of -0.19 and -0.15 eV for the 11 and 19 water molecules clusters, respectively, which must be compared with the isolated acrolein electronic transition energy of 3.90 eV. This red shift can be explained by the fact that, in these clusters, we have H-bonds involving the lone pairs of the carbonyl group of acrolein. Due to the shorter

distances, these H-bonds give the most important contribution to the solute-solvent Pauli repulsion interaction energy. In the $n \rightarrow \pi^*$ vertical transition, part of these electrons are moved to the CC double bond spatial region of acrolein, thus stabilizing the excited state as regards to the Pauli repulsion (red shift). For this reason, when there are H-bonds between solute and solvent molecules, the calculation of Pauli repulsion contribution to the electronic transition energy could be important. We expect that, in the absence of H-bonds or even stronger interactions, such effect will be smaller due to higher intermolecular distances.

For the future, we intend to improve the present approach by refining the model of the probe (here the solvent molecule).

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References

- [1] Cupellini L, Amovilli C, Mennucci B. *J. Phys. Chem. B* 2015; 119: 8984.
- [2] Warshel A, Levitt M. *J. Mol. Biol.* 1976; 103: 227.
- [3] Lin H, Truhlar D. *Theor. Chem. Acc.* 2007; 117: 185.
- [4] Senn H M, Thiel W. *Angew. Chem. Int. Ed.* 2009; 48: 1198.
- [5] Miertus S, Scrocco E, Tomasi J. *Chem. Phys.* 1981; 55:117.
- [6] Tomasi J, Persico M. *Chem. Rev.* 1994; 94:2027.
- [7] Floris FM, Tomasi J, Pascual Ahuir JL. *J. Comput. Chem.* 1991; 12: 784.
- [8] Amovilli C, Mennucci B. *J. Phys. Chem. B* 1997; 101:1051.
- [9] Bondesson L, Frediani L, Agren H, Mennucci B. *J. Phys. Chem. B.* 2006; 110: 11361.
- [10] Pomogaeva A, Chipman DM. *J. Phys. Chem. A* 2013; 117: 5812.
- [11] Marenich A, Cramer CJ, Truhlar DG. *J. Chem. Theory Comput.* 2013; 9: 3649.
- [12] Duignan TT, Parsons DF, Ninham BW. *J. Phys. Chem. B* 2013; 117: 9412.
- [13] Giovannini T, Lafiosca P, Cappelli C. *J. Chem. Theory Comput.* 2017; 13: 4854.
- [14] Curutchet C, Cupellini L, Kongsted J, Corni S, Frediani L, Steindal AH, Guido CA, Scalmani G, Mennucci B. *J. Chem. Theory Comput.* 2018; 14: 1671.
- [15] Amovilli C, McWeeny R. *Chem. Phys.* 1990; 140: 343.
- [16] Amovilli C, Floris FM. *J. Phys. Chem. A* 2015; 119: 5327.
- [17] Amovilli C, Floris FM. *8th MQM* (Uppsala, Sweden, 2016).
- [18] Guareschi R, Zulfikri H, Daday C, Floris FM, Amovilli C, Mennucci B, Filippi C. *J. Chem. Theory Comput.* 2016; 12: 1674.
- [19] Guareschi R, Floris FM, Amovilli C, Filippi C. *J. Chem. Theory Comput.* 2014; 10: 5528.
- [20] Floris FM, Filippi C, Amovilli C. *J. Chem. Phys.* 2014; 140: 034109.

- [21] Amovilli C, Filippi C, Floris FM. *J. Chem. Phys.* 2008; 129: 244106.
- [22] <http://www.utwente.nl/tnw/ccp/research/CHAMP.html>
- [23] Kitaura K, Morokuma K. *Int. J. Quantum Chem.* 1976; 10: 325.
- [24] Schmidt MW, Baldrige KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JA. *J. Comput. Chem.* 1993; 14: 1347.
- [25] Mackinney G, Temmer O. *J. Am. Chem. Soc.* 1948; 70: 3583.
- [26] Aidas K, Møgelhøi A, Nilsson EJK, Johnson MS, Mikkelsen KV, Christiansen O, Söderhjelm P, Kongsted K. *J. Chem. Phys.* 2008; 128: 194503.
- [27] Cammi R, Fukuda R, Ehara M, Nakatsuji H. *J. Chem. Phys.* 2010; 133: 024104.
- [28] Aquilante F, Barone V, Roos B. *J. Chem. Phys.* 2003; 119: 12323.
- [29] Muñoz-Losa A, Galvan IF, Aguilar MA, Martin E. *J. Phys. Chem. B* 2007; 111: 9864.

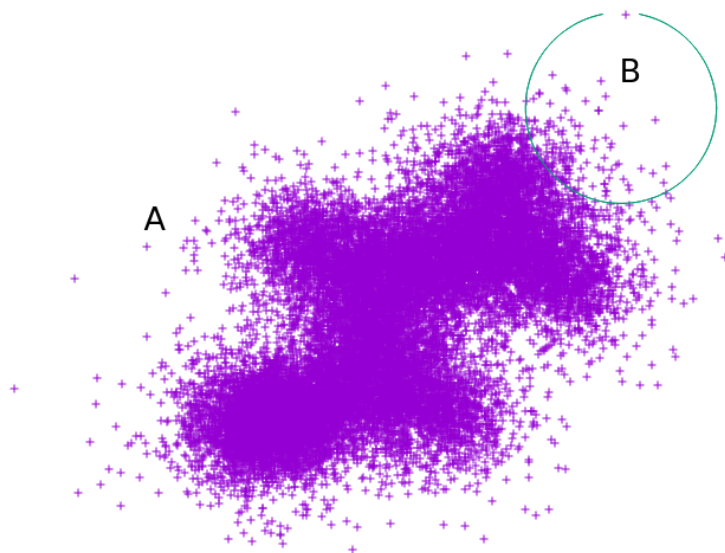


Figure 1: Schematic representation of the model used to compute the Pauli repulsion energy between the molecule of interest A and the probe B. The relevant contribution depends on the fraction of electrons of A found in the volume domain of B.

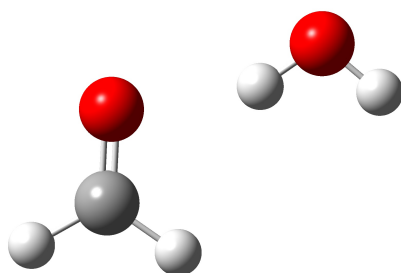


Figure 2: Formaldehyde water intermolecular complex.

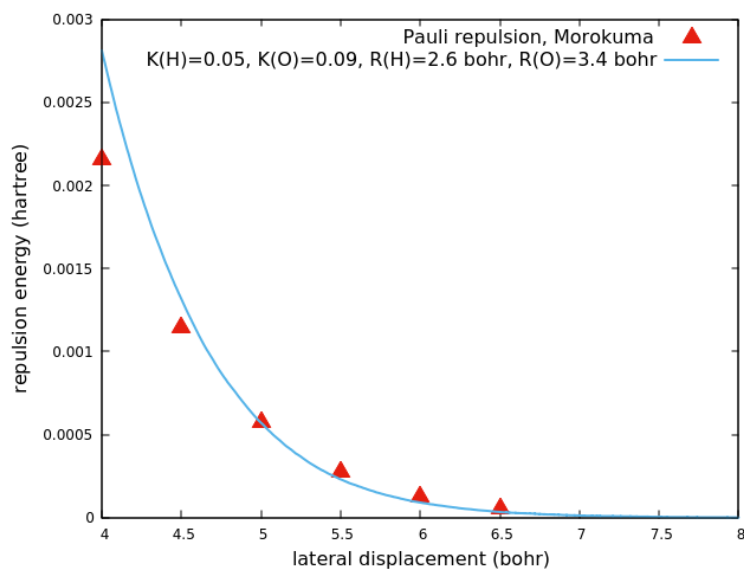


Figure 3: Formaldehyde water Pauli repulsion interaction as a function of water molecule displacement. Morokuma decomposition values (triangles) are compared with the model used in this work.

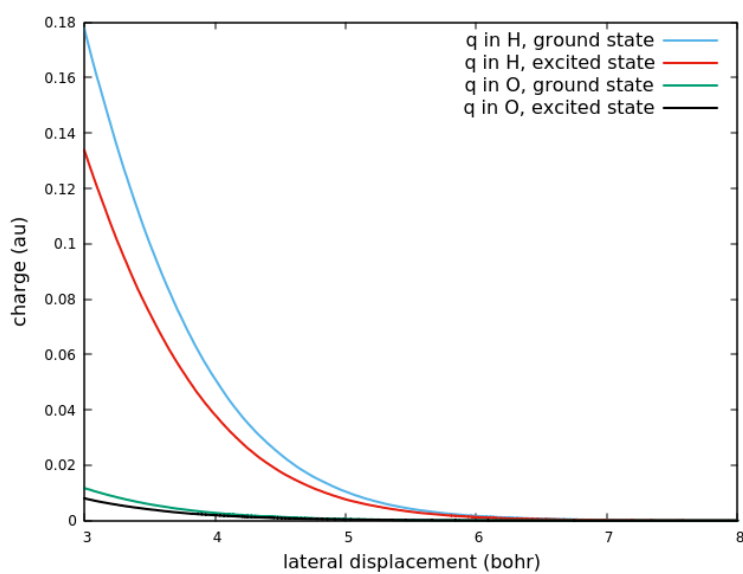


Figure 4: Formaldehyde electronic charge in the probe (water) domain as a function of water displacement for the ground state and the $n \rightarrow \pi^*$ excited state.

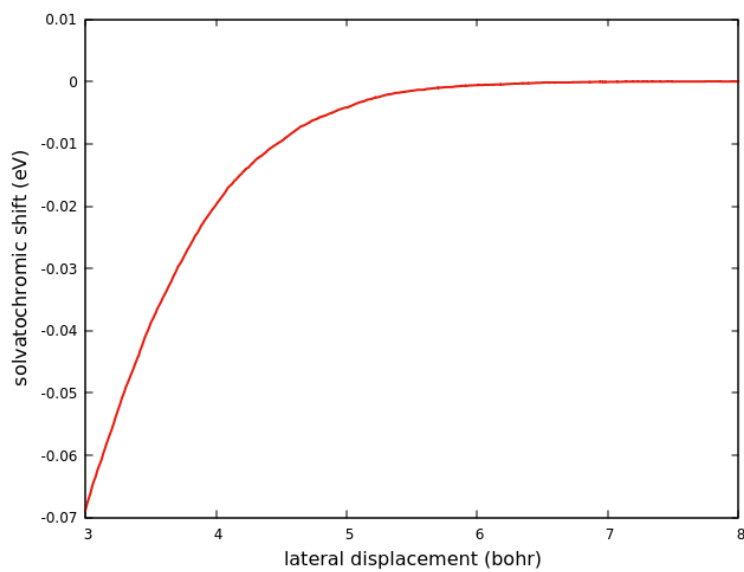


Figure 5: Transition energy shift due to Pauli repulsion in formaldehyde electronic $n \rightarrow \pi^*$ excitation as a function of water position.

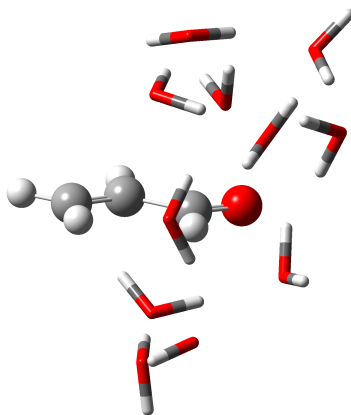


Figure 6: Cluster of acrolein solvated by 11 water molecules considered in this work.

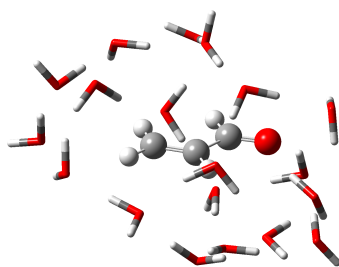


Figure 7: Cluster of acrolein solvated by 19 water molecules considered in this work.