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Dissecting the Hydrogen Bond: A Quantum Monte Carlo Approach

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Abstract: We present a Quantum Monte Carlo study of the dissociation energy and the dispersion curve of the water dimer, a prototype of hydrogen bonded system. Our calculations are based on a wave function which is a modern and fully correlated implementation of the Pauling's valence bond idea: the Jastrow Antisymmetrised Geminal Power (JAGP) [Casula et al. *J. Chem. Phys.* **2003**, *119*, 6500–6511]. With this variational wave function we obtain a binding energy of $-4.5(0.1)$ kcal/mol that is only slightly increased to $-4.9(0.1)$ kcal/mol by using the Lattice Regularized Diffusion Monte Carlo (LRDMC). This projection technique allows for the substantial improvement in the correlation energy of a given variational guess and indeed, when applied to the JAGP, yields a binding energy in fair agreement with the value of -5.0 kcal/mol reported by experiments and other theoretical works. The minimum position, the curvature, and the asymptotic behavior of the dispersion curve are well reproduced both at the variational and the LRDMC level. Moreover, thanks to the simplicity and the accuracy of our variational approach, we are able to dissect the various contributions to the binding energy of the water dimer in a systematic and controlled way. This is achieved by appropriately switching off determinantal and Jastrow variational terms in the JAGP. Within this scheme, we estimate that the dispersive van der Waals contribution to the electron correlation is substantial and amounts to $1.5(0.2)$ kcal/mol, this value being comparable with the intermolecular covalent energy that we find to be $1.1(0.2)$ kcal/mol. The present Quantum Monte Carlo approach based on the JAGP wave function is revealed as a promising tool for the interpretation and the quantitative description of weakly interacting systems, where both dispersive and covalent energy contributions play an important role.

1. Introduction

The hydrogen bond is a fundamental intramolecular and intermolecular interaction determining the properties of a

large number of systems from liquids to solids, from biological¹ to inorganic.² Hydrogen bond is commonly defined as a local bond in which a hydrogen atom is attached to an electronegative group (the donor) interacting with another nearby electronegative group (the acceptor) not covalently attached. Dissociation energies cover a range of about 2 orders of magnitude, ranging from -0.2 to 40 kcal/mol, the H-bonding arising from the interplay of different types of interactions. Electrostatic forces play the major role in a large number of hydrogen bonds, although charge transfer effects and van der Waals (vdW) interactions are always present.

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Water, the most studied H-bonding liquid, represents the prototype of hydrogen bonded systems. The energetics and directionality of water hydrogen bond is a key factor for understanding the anomalous properties of the water phase diagram,³ the behavior of small water clusters,^{4–6} and the role of aqueous environment in a variety of biological systems.⁷ The dissociation energy of the isolated water dimer lies in the middle of the hydrogen bond dissociation energy scale, the most stable configuration being associated with a binding energy $D_e^{\text{exp}} = -5.0$ kcal/mol, as extrapolated by experimental data.⁸ The partitioning of this energy in different contribution terms is still the subject of a vivid debate. At the equilibrium bonding distance, typically in a range between 2.5 and 3.5 Å, quantum effects become relevant, and a pure electrostatic picture of the interaction is not fully satisfactory. The partial covalent nature of the hydrogen bond has been recently invoked by the first analysis of the Compton profile on ice *lh*.⁹ However, the interpretation of the experimental data has been questioned by several authors^{10,11} and further revised.¹² The amount of the intermolecular covalent contribution, if any, to the binding energy is still an open issue. On the other hand, due to the lack of an unambiguous computational protocol it is still not clear how to estimate the van der Waals contribution to the hydrogen bonding. The role of these interactions may also be at the basis of the current drawbacks of empirical force fields in use for large scale simulations.^{13,14}

A definition of the intermolecular covalent component of the hydrogen bonding can be drawn using the intuitive picture of a chemical bond introduced by Pauling as the superposition of Lewis' structures.¹⁵ In the simple case of hydrogen bonding in a water dimer (H_2O)₂, three mesomeric Lewis structures may be drawn, one of them describing the charge transfer situation $(\text{OH})^-\cdots(\text{H}_3\text{O})^+$, that confers partial covalent character to the hydrogen bond. Within a quantitative Valence Bond representation it would be therefore possible to distinguish, in a simple way, the covalent intermolecular energy contribution by the other interaction energy terms.

At the same time, because of the crucial role of electronic correlation, especially for dispersive interactions, high quality electronic structure correlated methods (based on molecular orbital theory) are necessary for a proper quantitative description of a hydrogen bond. New classes of Density Functional Theory (DFT) functionals have been developed in the past years with the aim to describe weakly bound systems avoiding semiempirical approaches. Nevertheless, the highly nonperturbative and nonlocal character of the vdW interactions makes their inclusions difficult in DFT schemes without the resorting to ad hoc empirical parametrizations.¹⁶ Looking for an ab initio method free of empiricism, the Quantum Monte Carlo^{17,18} appears as a possible alternative to other more standard quantum chemistry methods such as Configuration Interaction, Möller Plesset perturbation theory, or coupled-cluster (CC).

Recently, a QMC technique based on the resonating valence bond wave function was introduced in ref 19 and further developed later. This approach represents a very efficient implementation of the valence bond Pauling idea,

discovered by P.W. Anderson in the field of strongly correlated electrons:²⁰ the Jastrow Antisymmetrized Geminal Power (JAGP). This wave function has been demonstrated to be effective in describing highly correlated diatomic molecules like the C_2 as well as π - π interacting complexes.^{17,19,21} In the present article we present a Variational Monte Carlo (VMC) and Lattice Regularized Diffusion Monte Carlo (LRDMC) study of the water dimer dissociation energy and dispersion curve, using as a variational ansatz the JAGP wave function. An important advantage of the JAGP VMC approach resides in the possibility of dissecting, in a simple way, the energy contributions of the different terms composing the wave function, like dynamical electron correlations and the intermolecular covalent contribution. Dynamical electronic correlations associated with the charge fluctuations and van der Waals interactions are indeed included in the wave function with Jastrow terms, whereas static correlations are described by the resonance of valence bond singlets in the AGP. The amount of binding energy arising from the correlated dynamical charge fluctuations, related to the vdW forces, can be therefore estimated by the evaluation of the energy contributions of the Jastrow factors. On the other side, following the Pauling idea of chemical bonding we can calculate the energy contribution of the intermolecular covalent term and get insight into the covalent nature of the hydrogen bonding mechanism.

2. Computational Methods

2.1. Geometries. For nuclear coordinates of the water monomer we used the experimental equilibrium geometry²² with an O–H bond length of 0.9572 Å and a H–O–H angle of 104.52°. For the dimer we used the linear configuration with C_s symmetry, oxygen–oxygen distance 2.976 Å,^{23,24} and $\text{O}_1\text{–H}_1\cdots\text{O}_2$ angle of 180°. We used the internal geometry of each monomer as the experimental one. For the dispersion curve we simply used the geometries obtained by shifting away the two monomers along the $\text{O}_1\text{–H}_1\cdots\text{O}_2$ binding axis and keeping fixed their relative orientation. Effects of nuclear relaxation upon binding do not affect our estimations, as we verified by calculating the binding energy with the geometry from CCSD(T) calculations.²⁵

2.2. Variational Monte Carlo and the JAGP Wave Function. As variational ansatz we use the JAGP wave function introduced in refs 19 and 21. The wave function Ψ_{JAGP} of a system of N electron is defined by the product of a symmetrical Jastrow term J and an antisymmetrical determinantal part Ψ_{AGP} :

$$\Psi_{\text{JAGP}}(r_1, \dots, r_N) = \Psi_{\text{AGP}}(r_1, \dots, r_N)J(r_1, \dots, r_N) \quad (1)$$

The determinantal part Ψ_{AGP} is the antisymmetrized product of spin singlets. The pairing function in singlet system without spin polarization is described by

$$\Psi_{\text{AGP}} = \hat{A}[\Phi(\mathbf{r}_1^\uparrow, \mathbf{r}_1^\downarrow)\dots\Phi(\mathbf{r}_{N/2}^\uparrow, \mathbf{r}_{N/2}^\downarrow)] \quad (2)$$

where \hat{A} is the operator that antisymmetrizes the product of $N/2$ geminal singlets $\Phi(\mathbf{r}^\uparrow, \mathbf{r}^\downarrow) = \psi(\mathbf{r}^\uparrow, \mathbf{r}^\downarrow)/\sqrt{2}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$. The spatial part of the geminals is expanded over an atomic basis set

$$\psi(\mathbf{r}^\uparrow, \mathbf{r}^\downarrow) = \sum_{a,b} \psi_{a,b}(\mathbf{r}^\uparrow, \mathbf{r}^\downarrow) \quad (3)$$

$$\psi_{a,b}(\mathbf{r}^\uparrow, \mathbf{r}^\downarrow) = \sum_{l,m} \lambda_{l,m}^{a,b} \phi_{a,l}(\mathbf{r}^\uparrow) \phi_{b,m}(\mathbf{r}^\downarrow) \quad (4)$$

where the indexes l, m run over different orbitals centered on nuclei a, b . The Jastrow factor J is further split into one-body, two-body, and three-body terms ($J = J_1 J_2 J_3$). The J_1 and J_2 terms deal with electron–electron and electron-ion correlation, respectively. The two-body (one body) Jastrow depends only on the relative distance $r_{i,j} = |\mathbf{r}_i - \mathbf{r}_j|$ between each electron pair (i, j) (electron-ion pair) and has been parametrized by a simple function $u(r_{i,j}) = (1 - \exp(-br_{i,j}))/2b$ that rapidly converges to a constant when $r_{i,j}$ became large.¹⁷ In this way the large distance behavior of the Jastrow is determined only by the J_3 Jastrow factor, that contains all variational freedom left and, in particular, as we shall see later on, the slowly decaying vdW correlations. Therefore we have chosen to parametrize this important part of our correlated wave function in a systematic and exhaustive way, similarly to what we have done for the AGP contribution:

$$J_3(\mathbf{r}_1, \dots, \mathbf{r}_N) = \exp\left(\sum_{i<j} \Phi^J(\mathbf{r}_i, \mathbf{r}_j)\right) \quad (5)$$

$$\Phi^J = \sum_{a,b} \Phi_{a,b}^J \Phi_{a,b}^J(r_i, r_j) = \sum_{l,m} g_{l,m}^{a,b} \phi_{a,l}^J(r_i) \phi_{b,m}^J(r_j) \quad (6)$$

Both the determinantal $\phi_{a,l}$ and Jastrow $\phi_{a,l}^J$ orbitals are expanded on Gaussian basis sets centered on the corresponding nuclear centers a and b . By increasing the atomic basis set one can rapidly reach the “complete basis set limit” because all cusp conditions are satisfied by an appropriate and simple choice of the J_1 (satisfying the electron-ion cusp) and J_2 (satisfying the electron–electron cusp) terms.¹⁷

All variational parameters, such as the Jastrow parameters and the $\{g\}$ and the $\{\lambda\}$ matrices of eqs 3 and 5 as well as the exponents and the coefficients of the Gaussian orbitals, have been optimized by energy minimization following the methods described in refs 26 and 27.

The oxygen valence-core interaction was described using the recently reported energy-consistent pseudopotentials.²⁸ A VMC calculation for the dimer system with the larger basis set and with 0.1 mH accuracy was run for about 12 h on eight AMD Opteron 280 CPUs at the CASPUR computer center. Full wave function optimization was about a factor of 4 more time-consuming.

2.3. Diffusion Monte Carlo. A systematic way for improving the quality of a variational wave function is to perform a Diffusion Monte Carlo calculation, filtering the ground-state properties by a diffusion process.²⁹ Actually, due to the presence of the fermionic problem, the DMC is implemented within the fixed node (FN) approximation,³⁰ by imposing that the final ground state has the same nodal structure of the trial WF. In this work we use a slightly modified version of the DMC method, the Lattice Regularized Diffusion Monte Carlo (LRDMC). In this method, the continuum Monte Carlo moves are made by discrete finite steps defined by two lattice spaces a and a' . By using an incommensurate ratio a'/a the electronic trajectory fills the entire space, thus avoiding most lattice artifacts. The

introduction of the lattice implies that there are a finite number of possible moves during the diffusion process, and this allows one to avoid the locality approximation and to restore the upper bound property of DMC.^{31,32} Within this regularization the exact Hamiltonian H is replaced by a lattice regularized one H_a such that $H_a \rightarrow H$ for $a \rightarrow 0$.³¹ We used as lattice spaces the values $a = 0.1, 0.2, 0.3, 0.5$ au, and then the energy was extrapolated to zero lattice space.

Since the dipole moment operator does not commute with the Hamiltonian, in LRDMC we evaluated the estimator $\mu = 2\mu_{LRDMC} - \mu_{VMC}$, where μ_{LRDMC} is the LRDMC mixed average value extrapolated to $a = 0$. A LRDMC calculation for the dimer system with the larger basis set, 0.1 mH accuracy and $a = 0.2$, was run for about 12 h on eight AMD Opteron 280 CPUs at the CASPUR computer center.

2.4. DFT Calculations. For the sake of comparison we perform DFT calculations using a plane wave basis set as implemented in the CPMD code.³³ For the exchange and the correlation part of the universal functional we used BLYP generalized gradient corrections^{34,35} and the hybrid functional B3LYP.³⁶ Core electrons were taken into account using norm-conserving Troullier-Martins type pseudopotentials.³⁷ We also performed calculations with Dispersion-Corrected Atom-Centered Potentials (DCACP)¹⁶ as described in ref 38. The Kohn–Sham orbitals were expanded in plane waves up to a cutoff of 125 Rydberg.

3. Results and Discussion

3.1. Dissociation Energy and Charge Fluctuations. In this section we report our results on the water dimer at the experimental binding distance, and we investigate the influence of different Jastrow terms of the wave function on the dissociation energy. In the pairing determinant the oxygen atoms are described using a Gaussian basis set of $4s4p$ contracted to $[1s2p]$, whereas we have only an uncontracted $1s$ shell for the hydrogen. We verified that the inclusion of a d -wave shell does not affect the binding energy giving only a rigid shift of the total energy of the dimer and the monomer within LRDMC.

On the contrary, more subtle effects have been observed in the structure of the three-body J_3 Jastrow factor. This term includes in the wave function additional dynamical electron correlations and contributes to the proper behavior of the electronic charge distribution. The correct description of the charge correlations reveals crucial for the inclusion of the dispersive contribution to the vdW interactions, being originated by the correlations between charge fluctuations in different spatial regions.³⁹

In Table 1 we report the JAGP monomer energy, $E_{\text{H}_2\text{O}}$, the dimer energy, $E_{(\text{H}_2\text{O})_2}$, and the dissociation energy, D_e , for increasing three-body Jastrow basis sets. The dissociation energy of the water dimer has been calculated simply as $D_e = E_{\text{dimer}} - 2E_{\text{monomer}}$. As the number of p -wave shells is increased, we observe an improvement of the binding energy, eventually obtaining at the VMC level a value of $D_e = 4.5(0.1)$ kcal/mol.

The reported LRDMC results, extrapolated to the $a = 0$ limit, appear to have a much faster convergence in terms of

Table 1. VMC and LRDMC Energies for the Water Monomer and Dimer (Atomic Units)^a

3-body Jastrow basis	$E_{\text{H}_2\text{O}}$	$E_{(\text{H}_2\text{O})_2}$	D_e
VMC			
2s2p-local[O]1s[H]	-17.2279(1)	-34.4585(2)	-0.0024(4)[-1.5(0.3)]
2s2p[O]1s[H]	-17.2388(2)	-34.4807(5)	-0.0031(7)[-1.9(0.4)]
2s4p[O]1s[H]	-17.24089(5)	-34.4874(1)	-0.0056(2)[-3.5(0.1)]
2s6p[O]1s[H]	-17.24119(8)	-34.4886(1)	-0.0062(4)[-3.9(0.3)]
2s6p[O]1s1p[H]	-17.2435(1)	-34.4940(1)	-0.0071(2)[-4.5(0.1)]
LRDMC			
2s2p-local[O]1s[H]	-17.2576(2)	-34.5228(2)	-0.0076(3)[-4.8(0.2)]
2s2p[O]1s[H]	-17.2613(1)	-34.5303(1)	-0.0077(2)[-4.8(0.2)]
2s4p[O]1s[H]	-17.2619(1)	-34.5315(1)	-0.0077(2)[-4.8(0.2)]
2s6p[O]1s[H]	-17.2619(1)	-34.5314(1)	-0.0076(2)[-4.8(0.1)]
2s6p[O]1s1p[H]	-17.2620(1)	-34.5318(1)	-0.0078(2)[-4.9(0.1)]

^a The dissociation energy calculated as $D_e = E_{(\text{H}_2\text{O})_2} - 2E_{\text{H}_2\text{O}}$ is reported in the last column in atomic units and (in square brackets) in kcal/mol.

total and dissociation energies. This is due to the nature of the projection method which accuracy relies only on the nodal surface of the trial wave function. Our results indicate that the VMC optimized nodal surface, and therefore the corresponding DMC energy, is only slightly affected by the basis set extension of the Jastrow factor. On the other hand, at the VMC level, the size of the Jastrow factor is crucial for improving the binding energy of the dimer. This is probably due to the role of the Jastrow in localizing charges and in introducing dynamical correlations. In this regard the role of *p*-wave shells in the binding energy will be discussed later in more details.

The LRDMC results are obtained extrapolating at zero lattice space and give a binding energy of 4.9 ± 0.1 kcal/mol, in good agreement with the high level quantum chemistry calculations: Klopper et al. have reported 4.99 kcal/mol and 5.02(5) kcal/mol, as a basis set limit for MP2 and Coupled Cluster calculations.²⁵ Recently a QMC study¹⁸ has reported a value of 5.4(1) kcal/mol, obtained without optimization of the orbitals in the determinant, which is directly taken from a B3LYP calculation.

Our LRDMC results are in the range of previously reported all-electron and pseudopotential QMC calculations.^{24,18,40} We also agree with experimental results although they suffer uncertainty due to theoretical estimation of the ZPE. Actually when compared with the experimental dimer dissociation energy D_e^{exp} , the difference between the zero point energy (ZPE) of the monomer and the dimer should be also taken into account: $D_e^{\text{exp}} = D_0 - 2ZPE^{\text{monomer}} + ZPE^{\text{dimer}}$. The experimental energy reported hereafter is therefore corrected by this quantity calculated by theory or estimated by experiments.²⁴ As pointed out in ref 17 the JAGP wave function is certainly size consistent for the two water monomers, only when the complete basis set limit is reached for the Jastrow factor. This property can be used to check the basis-set accuracy of the three-body Jastrow term. To verify the size consistency of the wave function we calculated the dissociation energy D_e^* by separating the two monomers by a large distance. D_e^* agrees with D_e .

In QMC calculations, correlation functions different from the energy are often very sensitive to the quality of a wave function. We have therefore calculated the monomer and dimer dipole moment μ that can be easily computed at the VMC level and at the LRDMC level using the mixed

Table 2. Dipole Moment of Water Monomer and Dimer^a

3B Jastrow basis	$\mu_{\text{H}_2\text{O}}$ [Debye]	$\mu_{2[\text{H}_2\text{O}]}$ [Debye]
VMC		
2s2p-local[O]1s[H]	2.116(17)	2.805(20)
2s2p[O]1s[H]	1.935(12)	2.834(23)
2s6p[O]1s[H]	1.880(8)	2.692(14)
2s6p[O]1s1p[H]	1.890(8)	2.597(12)
Extrapolated		
2s6p[O]1s[H]	1.874(10)	2.648(18)
2s6p[O]1s1p[H]	1.870(10)	2.603(13)

^a VMC estimates are reported in the top part of the table. Extrapolated values are reported in the bottom part of the table.

estimator. In the case of the water monomer both the variational and the LRDMC dipole moments are rather close to the experimental value of 1.855D.³ The correction introduced by LRDMC is a slight downshift of the extrapolated estimator, $\mu = 1.870(10) D$, in agreement with other QMC calculations¹⁸ and ab initio methods.⁴¹

We now turn our attention to the role of dynamical correlations included through the Jastrow term. As discussed above the inclusion of *p*-wave orbitals in the J_3 Jastrow term has a significant effect on the binding energy. Similarly, the effect of the J_3 basis set is also visible on the dipole moments in Table 2. One reason for this influence can be attributed to electrostatic interactions, since the 3-body term is important for the charge distribution. Another relevant effect of the J_3 term is the modulation of the van der Waals interactions. Three effects contribute to the van der Waals forces: induction, thermal orientation, and dispersion. The dispersion forces are quantum mechanical effects originating from the interaction between instantaneous dipoles or, using a second order perturbation theory perspective,⁴² by the correlated transition of a couple of electrons from occupied to unoccupied states. Given thus two atomic centers *a* and *b* at a large distance the J_3 term in eq 5 can be expanded for the small value of $g_{ij}^{a,b}$ and then applied to a single geminal pair (see eq 3), $\psi_{a,b}(r\uparrow, r\downarrow)$. The result can be viewed as a correlated transition of two electrons located in different atomic centers from occupied orbitals to unoccupied orbitals with higher angular momentum.⁴² More generally the effect of the J_3 at a large distance has the same structure of the vdW perturbative term if on each atomic center the basis used for the Jastrow contains odd orbitals with respect to the spatial reflection, namely when the Jastrow basis set

Table 3. VMC Energy and Dipole Moment of the Water Dimer for Different Jastrow J_3 Terms^a

pairing terms in J_3	$E_{(\text{H}_2\text{O})_2}$ (au)	ΔE kcal/mol	$\mu_{(\text{H}_2\text{O})_2}$ [D]
full $\{g_{l,m}^{a,b}\}$ matrix	-34.4940(1)	0.0	2.597(12)
(p[H]) ₁ (p[H]) ₂	-34.49372(9)	+0.2(1)	2.621(12)
(p[O]) ₁ (p[H]) ₂	-34.4938(1)	+0.1(1)	2.623(12)
(p[H]) ₁ (p[O]) ₂	-34.4935(1)	+0.3(1)	2.610(13)
(p[O]) ₁ (p[O]) ₂	-34.4918(1)	+1.4(1)	2.628(12)
intermolecular	-34.4916(3)	+1.5(2)	2.637(13)
$p-p$ $g_{l,m}^{a,b} = 0$			

^a The different J_3 are obtained by canceling the $p-p$ electronic correlation between atomic centers belonging to different molecules. The atomic center of the p wave is indicated between square brackets, and the water molecule index is indicated by the pedex (1 or 2). The energy difference ΔE with respect to the complete $g_{l,m}^{a,b}$ matrix, first line, is also reported in kcal/mol.

contains at least p wave orbitals. In principle a small vdW contribution can be derived also from high angular momentum orbitals included in the geminal expansion. In this work however, in order to disentangle the genuine dispersive vdW contribution, we have avoided using polarization orbitals in the AGP that, as discussed before, do not affect the binding energy. In this way the instantaneous correlated polarization induced by the J_3 term allows for the inclusion of dispersive vdW interactions in a transparent variational form.

To understand the effects of the J_3 terms on the dissociation energy, we calculated the variational energy of the wave function obtained excluding intermolecular $g_{l,m}^{a,b}$ terms in eq 5 as reported in Table 3. In particular we considered the H–O and O–O contributions in the $p-p$ channel, and eventually we eliminated all intermolecular terms (last row of Table 3). Data show nonadditivity of the energy loss, as expected by interactions arising from polarization effects.⁴³ Among the $p-p$ wave contribution, the oxygen–oxygen channel seems to be the most relevant term in the Jastrow expansion. It is worth noting that the total dipole moment of the dimer depends only weakly on the intermolecular J_3 Jastrow terms, see Table 3. This indicates that the distribution of the electronic charge is not greatly affected by the missing terms. The energy differences are then due to the part of the dynamical correlation involving correlated excitations to p states. The energy loss in the binding energy can therefore be attributed within our formalism to dispersive van der Waals interactions.

It is of interest to compare our result to previous calculations based on symmetry-adapted-perturbation-theory (SAPT)^{44,45} that estimated the contribution of dispersion forces to the water dimer hydrogen bond. This contribution amounts to about -1.75 kcal/mol as reported in Table 5 of ref 45. Albeit the energy is not partitioned the same way in the two approaches, the assessment given by SAPT is in good agreement with our estimation of $-1.5(2)$ kcal/mol.

3.2. Dispersion Curve. The VMC and LRDMC dispersion curve of the water dimer is reported in Figure 1A. It has been calculated by computing the total dimer energy as a function of the oxygen–oxygen distance without changing the internal geometry and the relative orientation of the monomers. We used the 2s6p[O]1s[H] basis set for the 3-body Jastrow, which, as reported before, guarantees size consistency during the dissociation process at large distances.

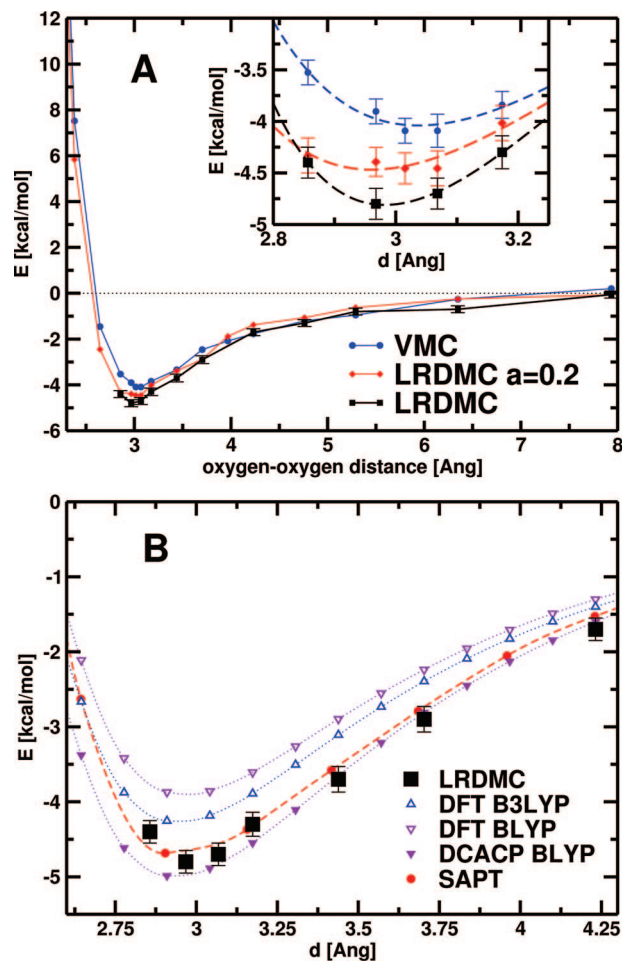


Figure 1. Water dimer dissociation. The total energy of the water dimer is reported as a function of the oxygen–oxygen distance. In Panel A the VMC and LRDMC results are reported. In the inset graph the behavior around the minimum is zoomed in. In Panel B the LRDMC curve is compared with other methods. SAPT values have been taken from ref 46.

The attractive tail of the water–water interaction potential is dominated by a dipole–dipole interaction energy. A polynomial fit for $d \geq 3.5$ Å shows that $E_{2(\text{H}_2\text{O})} \sim d^\alpha$ with $\alpha = 3.2-3.3$ for the VMC and the extrapolated LRDMC curves, respectively.

The behavior of the dispersion curve at short distances is shown in the inset of Figure 1A, together with a fit performed using a Morse potential. At the VMC level, the minimum of the curve, as obtained by the fitting procedure, is at distance $d = 3.037(4)$ Å, which is slightly shifted with respect to $d = 2.976$ Å reported by experiments.²³ However, it should be noted that, considering the error bars, the curve results to be rather flat around the equilibrium distance. LRDMC with a lattice space $a = 0.2$ au, and the LRDMC extrapolation to zero lattice space $a \rightarrow 0$, improves the location of the equilibrium distance. In this latter case the fitted minimum is at $d = 2.982(1)$ Å, which is very close to the experimental value. In Figure 1B we report a comparison with pure or empirically parametrized Density Functional methods and symmetry-adapted perturbation theory (SAPT).^{44,46} Data show that pure BLYP and B3LYP curves underestimate the dissociation energy, whereas calculations performed with

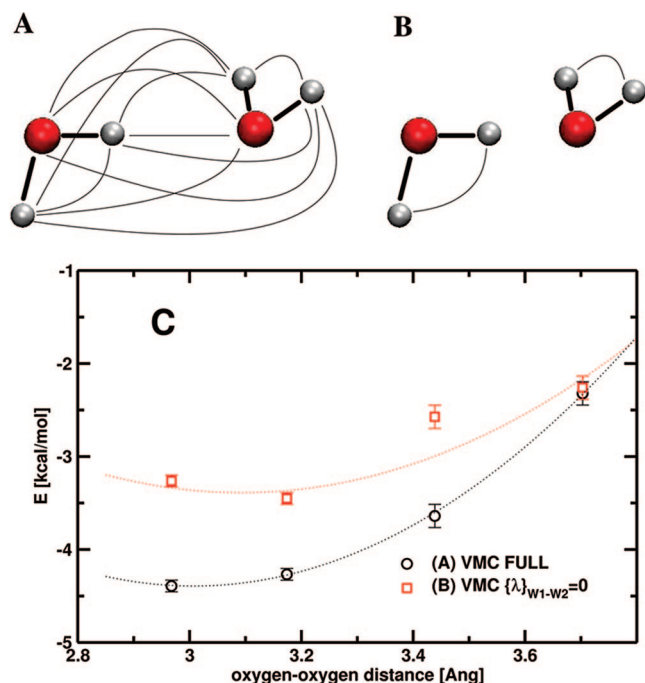


Figure 2. Top panel: Pictorial view of the intermolecular pairing term of the determinant part of the wave function. In Panel A all the intermolecular pairing are drawn. In Panel B we represent the wave function with the intermolecular pairing term set to zero. In the bottom part of the figure the total energy of the water dimer is reported as a function of the oxygen–oxygen distance between the two monomers. Two wave functions are compared, one with all the intermolecular pairing term optimized (black circle) and the other one with intermolecular pairing terms set to zero (red square).

empirically parametrized DCACP pseudopotentials are closer to our LRDMC curve. The SAPT curve is at the top of our results with small discrepancies at very short distance.

3.3. Covalent Contribution to Hydrogen Bonding. In the proximity to the equilibrium distance the interplay between electrostatic and pure quantum effects is expected to be relevant. Although a unique and commonly accepted definition of covalent contribution in a hydrogen bond is still missing, within the formalism of the JAGP wave function, we can define the covalent energy contribution as the energy contribution arising from the intermolecular pairing terms of the RVB determinantal part of the wave function (see eq 3).

The “chemical bond” between the two molecules is indeed due to the superposition of all singlet terms in the geminal expansion that connect two nuclei belonging to different water molecules. This is schematically illustrated in the panel A of Figure 2. In order to evaluate the covalent contribution we proceed as follows. We cut the intermolecular pairing valence bonds in the pairing function, by imposing $\psi_{a,b} = 0$ if a and b belong to different monomers (as sketched in panel B of Figure 2). Then the wave function is reoptimized with the above constraint in order to correctly include the electrostatic effects and the slowly decaying vdW correlations present in our Jastrow factor. In Figure 2C we report, as a function of the oxygen–oxygen distance, the binding energy calculated with the full wave function (circle) and with the wave function lacking the intermolecular valence bond terms

(square). The difference between the two curves vanishes as the molecules reach a O–O distance of 3.5 Å. We point out that, by cutting the intermolecular pairing terms, the minimum of the energy dispersion slightly shifts to a larger equilibrium distance.

At the equilibrium distance we found that the contribution of the intermolecular pairing terms, computed at the VMC level, is $\Delta_{inter} = 1.1(0.1)$ kcal/mol, corresponding to about 24% of the computed dimer binding energy. Our estimate of the covalent contribution, defined above, can be compared to what other authors found using different theoretical frameworks and different definition and that is generally referred to as intermolecular charge transfer (CT).^{47–50} In the seminal works based on Morokuma decomposition of the binding energy^{47,48} the CT contribution to hydrogen bonding is estimated in the range -1.3 to -1.8 kcal/mol, thus about 25% of the total binding energy. A slight smaller contribution, about 11%, resorts from the block-localized wave function approach proposed by Mo et al.⁴⁹ They also reported that CT contribution vanishes at about 3.5 Å in good agreement with our finding. It is interesting to observe that the damping of the oscillation at $d \sim 4$ Å of the Fourier Transforms of the Compton profile has been interpreted in ref 12 as a cutoff for the covalent contribution.^{9,12} However such an interpretation of the experiments is not fully accepted.^{10,11}

4. Conclusions

The understanding of hydrogen bond systems is still a challenge for computational chemistry. Even for small molecular systems the weakness of the interactions and the critical role of electron correlation require the use of affordable correlated quantum chemistry methods. The interplay between interactions different in nature, such as dispersion forces and intermolecular charge transfer, is in many cases crucial for the proper description of the bond properties.

We have shown that the Quantum Monte Carlo method is effective for describing the hydrogen bond between two water molecules. The calculated binding energy matches the experimental value and the estimates from other advanced methodologies. Good agreement with experiments is also achieved for the computed dipole moments. Thanks to the good size scaling properties and the embarrassingly parallelism of QMC algorithms, these methods appear extremely competitive in the context of massive parallel computation.

Moreover, some conceptual advantages rely on the structure of the AGP wave function, a correlated valence bond representation of the electronic system. The AGP formalism gives the possibility to work back on an intuitive picture of localized chemical bonds such as the Pauling’s superposition of Lewis structures. Thanks to the fully correlated structure of the wave function, this picture can be used without compromises in terms of accuracy.

Upon interpretation of the wave function terms, we estimate at the VMC level the covalent contribution to account for 1.1(2) kcal/mol. A similar contribution to the binding energy is given by correlated dipolar vdW fluctuations that account for 1.5(2) kcal/mol.

The quality of our results on the water dimer encourages the application of the method to larger hydrogen bonded systems such as water clusters or small biomolecules. To reduce the computational costs it would be desirable to keep down the number of variational parameters when the size of the system increases. In this respect, different strategies are under investigation.

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