Resonating Valence Bond Quantum Monte Carlo: Application to the ozone molecule

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We study the potential energy surface of the ozone molecule by means of Quantum Monte Carlo simulations based on the resonating valence bond concept. The trial wave function consists of an antisymmetrized geminal power wave function arranged in a single-determinant that is multiplied by a Jastrow correlation factor. Whereas the determinantal part incorporates static correlation effects, the augmented real-space correlation factor accounts for the dynamics electron correlation. The accuracy of this approach is demonstrated by computing the potential energy surface for the ozone molecule in three vibrational states: symmetric, asymmetric and scissoring. We find that the employed wave function provides a detailed description of rather strongly-correlated multi-reference systems, which is in quantitative agreement with experiment.

I. INTRODUCTION

Beside its environmental and chemical importance, ozone plays a significant role in assessing the accuracy of electronic structure methods due to its multi-reference character. The latter is due to static electron correlation that arises in situations with degeneracy or near-degeneracy, as in transition metal chemistry. As a consequence, determining the electronic structure methods due to its multi-reference character. The latter is due to static electron correlation that arises in situations with degeneracy or near-degeneracy, as in transition metal chemistry.

In this work, we study the potential energy surface (PES) of a single O₃ molecule using the resonating valence bond (RVB) theory of the chemical bond, which was first introduced by Pauling in the early days of quantum mechanics. According to the RVB theory, a spin singlet can be formed between any two valence electrons belonging to neighboring atoms. Within this approach, the ground state wave function of a molecule can lower the variational energy by imposing an auxiliary resonating degree of freedom between all valence bond configurations. However, the number of bonds increases exponentially with the number of atoms. Nevertheless, it was realized that a single-determinant wave function combined with a suitable real space correlation term, known as the Jastrow correlation factor, can be employed to represent a complex RVB state. To that extend, the variational energy is computed by means of conventional QMC techniques, such as variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC). The RVB wave function is expanded in terms of molecular orbitals (MOs) and optimized by a constrained energy minimization at constant number of MOs. In this way, an accurate RVB wave function based on a single-determinant is obtained, which allows to study systems with sizable static and dynamic electron correlation.

II. RESONATING VALENCE BOND QUANTUM MONTE CARLO

The RVB wave function, which is referred to as Jastrow antisymmetrized geminal power (J-AGP), is given by a product of a Jastrow correlation factor and a determinantal part \( \Phi_N \), i.e. \( \Psi_{\text{J-AGP}} = J \Phi_N \). Each geminal is described by a symmetric pairing-function \( \phi(r_i, r_j) = \phi(r_j, r_i) \). For an \( N \) electron system, consisting of \( N^+ \) spin-up and \( N^- \) spin-down electrons and assuming that \( N^- \leq N^+ \), we can define a pure spin state with total spin \( S = (N^+ - N^-)/2 \) and maximum spin projection \( S_z = S_{\text{tot}} \) in terms of an antisymmetrized product of \( N^- \) singlet pairs and \( 2S \) unpaired orbitals \( \phi_j(r_j^+) \) of the remaining spin-up electrons. The resulting antisymmetrized geminal power (AGP) wave function, which can be arranged in a single-determinant form, reads as

\[
\Phi_N(R) = A \prod_{i=1}^{N^+} \phi(r_i^+, r_i^-) \prod_{j=N^++1}^{N^*} \phi_j(r_j^+),
\]
From this it follows that Eq. (3) is equivalent to a diagonal matrix, the particular basis set used are implicitly dependent on the previously introduced pairing-function $\phi(r_i, r_j)$ and is chosen such to satisfy the Kato cusp condition.

Just like any other function of two coordinates, $f(r_i, r_j)$ as well as $\phi(r_i, r_j)$ can be expressed in terms of single-particle orbitals:

$$\phi(r_i, r_j) = \sum_{a,b} \sum_{\mu, \nu} \lambda_{a,b} \varphi_{\mu}(r_i) \varphi_{\nu}(r_j),$$

where $\varphi(r)$ is an atomic orbital (AO), while $m$ is the number of AOs per atom and $M$ the number of atoms. The coefficients $\lambda_{a,b}$ are arranged in a quadratic $mM \times mM$ matrix denoted as $\Lambda$. Moreover, to conserve the total spin, $\Lambda$ is also symmetric. Assuming that the AOs are non-orthogonal, i.e. $S_{a,b} = \langle \varphi | \varphi \rangle \neq I$, diagonalizing $\Lambda$ corresponds to solving the equation

$$ASP = PA',$$  

where the matrix $P$ contains the eigenvectors of $\Lambda$ and diagonal matrix $A'$ the associated eigenvalues $|\lambda_1|^2 \geq |\lambda_2|^2 \cdots |\lambda_{mM}| \geq 0$. The number of non-zero eigenvalues is equivalent to the rank of $\Lambda$. Using the identity $P^T SP = I$ that is identical to $(SP)^{-1}$ and multiplying it to the right of Eq. (4), $\Lambda = PA'P^T$ is obtained. From this it follows that Eq. (3) is equivalent to

$$\phi(r_i, r_j) = \sum_{k=1}^{n-2S} \lambda_k \phi_k(r_i) \phi_k(r_j),$$

where $n$ is the number of MOs $\phi_k(r_i)$ that can be written as a linear combination of AOs:

$$\phi_k(r_i) = \sum_{l} c_{kl} \varphi_l(r_i),$$

where $c_{kl}$ are the AO coefficients that independently on the particular basis set used are implicitly dependent on $r_i$.

The smallest number of orbitals, which is compatible with an unpolarized $N$-electron system, is $n = N^\uparrow$. In that case the rank of $\Lambda$ is also minimal and identical to $n$ and the antisymmetrization operator $A'$ singles out just one Slater determinant (SD). Due to the fact that the determinantal part of the resulting wave function is equivalent to the one of unrestricted Hartree-Fock (HF) theory, we will refer to it as JHF to emphasize the presence of the Jastrow correlation factor. If the orbitals of the SD are determined by means of density functional theory (DFT), the eventual wave function is denoted as JDFT. However, the great appeal of the AGP wave function is that if the rank of $\Lambda$ is larger than $N^\uparrow$, it corresponds to a multireference wave function that is able to describe static electron correlation effects, although at the computational cost of a genuine single-determinant approach. We will name the resulting wave function as JAGP. As such, the RVB wave function can be thought of as the natural extension of the HF theory, where the Jastrow correlation factor accounts for the dynamic electron correlation, while for $n > N^\uparrow$ most of the static correlation is recovered.

### III. COMPUTATIONAL DETAILS

All of our QMC calculations were performed using the TurboRVB program package of Sorella and coworkers.\cite{Sorella1995}

We have employed the two different trial wave functions, the JDFT and the JAGP wave function. In both cases the single-determinant is made of MOs as obtained by DFT within local-density approximation (LDA), as described in Ref. \cite{Sorella1995}. In case of the JAGP wave function all parameters were variationally optimized at the VMC level of theory using the stochastic reconfiguration algorithm,\cite{Sorella1995} while for the JDFT wave function the parameters of the Jastrow factor were held fixed. Scalar-relativistic energy consistent pseudopotentials\cite{Sorella1995} were used to describe two core electrons of the oxygen atoms. For the single-determinant we employed an atomic basis set consisting of contracted 10s, 8p, 6d, 4f Gaussian-type orbitals, while for the Jastrow correlation factor uncontracted 2s, 2p, 1d Gaussian-type orbitals were used. The variational energies were computed using two different QMC methods, VMC and the even more accurate lattice-regularised diffusion Monte Carlo (LRDMC) projection technique,\cite{Sorella1995}, which eventually results in four trial wave functions we have investigated here: JDFT-VMC, JDFT-LRDMC, JAGP-VMC and JAGP-LRDMC.

### IV. RESULTS AND DISCUSSION

The PES of the $O_3$ molecule exhibits two types of minima, one of $C_{2v}$ symmetry (open minimum) with an apex angle of 116.75° and another one of $D_{3h}$ symmetry (ring minimum), where the oxygen atoms form an equilateral
triangle. Due to the fact that the open structure is energetically significantly lower than the closed ring case, we will confine ourselves to the $O_3$ molecule with $C_{2v}$ symmetry only. Symmetry considerations suggest the existence of three open minima, which are separated by energetically high barriers and thus can be considered as independent from each other. As a consequence, the potential energy $E(d_1, d_2, \alpha)$ is calculated as a function of just three variables, where $d_1$ and $d_2$ are the two $O_c$–$O$ bond distances, while $\alpha$ is the $O$–$O_c$–$O$ bond angle and $O_c$ the central atom. The experimental values for $d_1$, $d_2$, $\alpha$, and the dissociation energy are 2.4052\AA, 2.4052\AA, 116.75°, and 26.10 kcal/mol, respectively.

Figure 1 illustrates the PES of the $O_3(\tilde{X})$ molecule in a symmetrical vibration state, where the value of $\alpha$ is fixed at 116.8° and the $d_1 = d_2$. The compressed $O_3(\tilde{X})$ molecule is dominated by Coulomb repulsion and the results of all trial wave functions investigated here rather similar. However, whenever the $O_3(\tilde{X})$ molecule is stretched, static electron correlation becomes more important and the JAGP wave function superior due to the strong multi-reference character of the stretched $O$–$O$ bond. The dissociation energies at the experimental equilibrium geometry, using the JDFT-VMC, JDFT-LRDMC, JAGP-VMC, as well as JAGP-LRDMC methods are $-16.60(5), -19.74(4), -25.25(6)$ and $-26.14(5)$ kcal/mol, respectively. In fact, even in at the variational level, the JAGP wave function outperforms accurate LRDMC calculations based on the JDFT trial wave function and recovers ~97% of the experimental dissociation energy, while at the JAGP-LRDMC level the result is correct up to 0.1%.

The PES of the $O_3(\tilde{X})$ molecule in an asymmetrical stretching state is shown in Figure 2, where the value of $\alpha$ is again fixed at 116.8°. Defining $\delta d$ as deviation from the equilibrium bond length, each point on the PES corresponds to $d_1 \pm \delta d$ and $d_2 \mp \delta d$. Given the symmetry, $E(d_1 + \delta d, d_2 - \delta d, \alpha) = E(d_1 - \delta d, d_2 + \delta d, \alpha)$, as can been seen in the axial symmetry around the equilibrium bond length in Figure 2. The corresponding dissociation energies for the JDFT-VMC, JDFT-LRDMC, JAGP-VMC, as well as JAGP-LRDMC techniques are $-16.58(6), -19.71(5), -24.99(7)$ and $-25.64(5)$ kcal/mol, respectively. Interestingly, at equilibrium the JAGP is significantly superior to the JDFT trial wave function regardless of the particular QMC method, whereas for large asymmetries the LRDMC technique is essential.
Figure 3 exhibits the PES of the \( O_3(\tilde{X}) \) molecule in a scissoring state, where \( d_1 \) and \( d_2 \) are both fixed at 2.4052\( a_0 \) and, thus, \( \alpha \) the only variable. At the equilibrium bond angle, the dissociation energies as obtained by the JDFT-VMC, JDFT-LRDMC, JAGP-VMC and JAGP-LRDMC methods are -17.42(7), -20.55(5), -25.61(6), and -25.97(5) kcal/mol, respectively. Again, the JAGP systematically improves the description of the JDFT wave function. In fact, even at the JAGP-VMC method exceeds JDFT-based LRDMC calculations. Moreover, the small difference between the JAGP-VMC and JAGP-LRDMC schemes clearly demonstrates accuracy of the JAGP approach.

V. CONCLUSIONS

In summary, we find that the JAGP systematically improves upon the conventional JDFT wave function in all cases we have considered here. In particular, except for the most asymmetric configurations, the JAGP-VMC method was able to outperform even more accurate LRDMC calculations based on the JDFT trail wave function. Together with the fact that the differences between the JAGP-VMC and JAGP-LRDMC results were rather small, this is a clear manifestation of the superiority of the JAGP wave function. In any case, the significant deviation between the JDFT and JAGP trail wave functions highlights that for a multi-reference system, such as the \( O_3(\tilde{X}) \) molecule, an accurate treatment of static electron correlation effects is essential.
A. Lüchow, WIREs Comput. Mol. Sci. 1, 388 (2011).
B. M. Austin, D. Y. Zubarev and W. A. Lester, Chem. Rev. 112, 263 (2012).
W. L. McMillan, Phys. Rev. 138, A442 (1965).
D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).
M. Marchi, S. Azadi, M. Casula and S. Sorella, J. Chem. Phys. 131, 154116 (2009).
M. Casula, M. Marchi, S. Azadi and S. Sorella, Chem. Phys. Lett. 477, 255 (2009).
M. Marchi, S. Azadi and S. Sorella, Phys. Rev. Lett. 107, 086807 (2011).
S. Azadi, W. M. C. Foulkes and T. D. Kühne, New J. Phys. 15, 113005 (2013).
S. Azadi, B. Monserrat, W. M. C. Foulkes and R. J. Needs, Phys. Rev. Lett. 112, 165501 (2014).
M. Casula and S. Sorella, J. Chem. Phys. 119, 6500 (2003).
M. Casula, C. Attaccalite and S. Sorella, J. Chem. Phys. 121, 7110 (2004).
A. C. Hurley, J. E. Lennard-Jones and J. A. Pople, Proc. R. Soc. A 220, 446 (1953).
J. Bardeen, L. N. Cooper and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).
G. K.-L. Chan, WIREs Comput. Mol. Sci. 2, 907 (2012).
T. Kato, Comm. Pure Appl. Math. 10, 151 (1957).
S. Azadi, C Cavazzoni, and S. Sorella, Phys. Rev. B 82, 125112 (2010).
S. Sorella, TurboRVB Quantum Monte Carlo package
S. Sorella, Phys. Rev. B 71, 241103(R) (2005).
S. Sorella, M. Casula and D. Rocca, J. Chem. Phys. 127, 014105 (2007).
F. Calcavecchia and T. D. Kühne, arXiv:1501.01428 (2015).
M. Burkatzki, C. Filippi, and M. Dolg, J. Chem. Phys. 126, 234105 (2007).
M. Casula, C. Filippi, and S. Sorella, Phys. Rev. Lett. 95, 100201 (2005).
R. Siebert, P. Fleurat-Lessard, R. Schinke, M. Bittererova, and S. C. Farantos, J. Chem. Phys. 116, 9749 (2002).
Vl. G. Tyuterev, S. Tashkun, D. W. Schwenke, P. Jensen, T. Cours, A. Barbe, and M. Jacon, Chem. Phys. Lett. 316, 271 (2000).