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Assessing the accuracy of the Jastrow antisymmetrized geminal power in the H_4 model system

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ABSTRACT

We report a quantum Monte Carlo study, on a very simple but nevertheless very instructive model system of four hydrogen atoms, recently proposed in Gasperich *et al.* [J. Chem. Phys. **147**, 074106 (2017)]. We find that the Jastrow correlated Antisymmetrized Geminal Power (JAGP) is able to recover most of the correlation energy even when the geometry is symmetric and the hydrogens lie on the edges of a perfect square. Under such conditions, the diradical character of the molecule ground state prevents a single determinant *Ansatz* to achieve an acceptable accuracy, whereas the JAGP performs very well for all geometries. Remarkably, this is obtained with a similar computational effort. Moreover, we find that the Jastrow factor is fundamental in promoting the correct resonances among several configurations in the JAGP, which cannot show up in the pure Antisymmetrized Geminal Power (AGP). We also show the extremely fast convergence of this approach in the extension of the basis set. Remarkably, only the simultaneous optimization of the Jastrow and the AGP part of our variational *Ansatz* is able to recover an almost perfect nodal surface, yielding therefore state of the art energies, almost converged in the complete basis set limit, when the so called diffusion Monte Carlo is applied.

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I. INTRODUCTION

In recent years, much progress has been made in the definition of variational wave functions (WFs) capable to describe rather accurately the electron correlation. For this purpose, two strategies have been employed: (i) the use of multi-determinant wave functions[2–4] and (ii) exploiting the large variational freedom that can be achieved by applying a correlation term, dubbed Jastrow factor (JF), to a generic pairing function.[5–7] Even if the latter approach cannot be systematically improved, it may open the way to deal with large systems, thanks to the moderate scaling with the number of electrons. Indeed, the corresponding correlated WF can be simulated efficiently within a statistical method, based on quantum Monte Carlo (QMC).[8] Thanks to well established advances[9,10] in this field, it is possible nowadays to compute the total energy of a given correlated *Ansatz* and to optimize several variational parameters with a computational effort scaling at most with the fourth power of the number of electrons.

A good variational *Ansatz* allows a good description of the ground state by energy optimization. Moreover, an even better characterization can be obtained by applying the so called diffusion Monte Carlo (DMC) method with the fixed node approximation (FNA).[11,12] Within this projection method, it is possible to obtain the lowest energy state constrained to have the same signs of a chosen trial WF, in the configuration space where electron positions and spins are given. The connected regions of space with the same sign are called nodal pockets and the surface determining these pockets, satisfying

WF = 0, the nodal surface. Usually, the energy optimization, implemented here, has been shown to be very successful to determine the nodal surface of the WF as we will also show in the present study. In this work, we have used a particular method for implementing the FNA which is called lattice regularized diffusion Monte Carlo (LRDMC).[13] While usually a short imaginary time approximation is applied to the propagator for its finite time evaluation, in the LRDMC, a lattice regularization is employed in the physical space by using a finite mesh approximation.[14]

A widely used *Ansatz* for the WF is the single Slater determinant (SD). The SD can be taken directly from Hartree-Fock (HF) or density functional theory (DFT) calculations without further optimizations. Unfortunately, this approach can fail to describe the exact ground state WF and its nodes, and therefore, a more complex procedure is often required. Depending on the problem, it may be necessary to further optimize the SD parameters or to change the *Ansatz*. Instead of the SD, it is possible to consider more advanced WF using multideterminant *Ansätze* within, for instance, Full Configuration Interaction (FCI) or Complete Active Space CAS (*n*, *m*), with *n* active electrons in *m* orbitals, or a more accurate single determinant Geminal WF antisymmetrized geminal power (AGP).[5,15–19] It is well known that it is possible to improve considerably the correlation energy by multiplying a given *Ansatz* by a JF. The WF built with an AGP and a JF is indicated as Jastrow correlated antisymmetrized geminal power (JAGP), while the SD and the JF are indicated as Jastrow Slater Determinant (JSD). Once the *Ansatz* of the WF is given, it is also important to choose an appropriate atomic basis set. Enlarging the basis set allows us to be closer to the complete basis set (CBS) limit, but at the same time increases the number of variational parameters. It is therefore important to have a compact description of the WF by using an atomic basis set as small as possible.

Even relatively simple systems can hide pitfalls that can be very difficult to solve. The case of the $(H_2)_2$, a system of two diatomic molecules of hydrogen at equilibrium distance, first introduced in QMC literature by Anderson,[20,21] is emblematic from this point of view: as recently shown by Gasperich *et al.*,[1] a single SD can only give a very poor description of this system when it approaches the square geometry. This is due to the degeneracy of the frontier orbitals in the square limit that a single SD is not able to reproduce. In this paper, we show that a single AGP determinant enriched with the JF correlator allows a perfect description of the ground state.

The simplicity of this model system allows us to study the role of the optimization in determining an accurate nodal surface because, by repeating several times the optimization, we can be safely confident that the absolute minimum energy WF is obtained. On the other hand, we can also verify that our stochastic optimization[22] works also when we remove the Jastrow from our *Ansatz*, providing the lowest energy AGP, clearly with much larger computational effort compared to deterministic methods that, to our knowledge, are not available for the AGP. This tool has been proved to be very useful in this work because we are able to show that the use of a pure AGP determinant (without any JF) can give

rise not only to a poor description of the electronic correlation but also a qualitatively wrong picture of the chemical bond.

Moreover, similarly to what found in the benchmark study of the hydrogen chain,[23] the fulfillment of the electron-electron and electron-ion cusp conditions, obtained with a suitably chosen JF, makes the convergence to the CBS particularly fast and efficient, requiring only a double zeta gaussian basis set (cc-pVDZ) for the accurate description of the corresponding nodal surface. Remarkably, the DMC energies obtained with the double zeta JAGP trial WF are better than the ones obtained with the CAS(2,2) and CAS(4,4) and also with the full configuration interaction (FCI) calculated with a quadruple zeta basis.[1]

II. WAVE FUNCTIONS AND PROCEDURE

For this study, we used WFs given by the product of a determinant, SD or AGP, and a JF, optimized with standard stochastic techniques.[13] For all the calculations, we used the TurboRVB package.[24]

The value of the WF for an electronic configuration **X** is given as

$$\langle \mathbf{x} | \Psi \rangle = \Psi(\mathbf{X}) = J(\mathbf{X}) \times \Psi_{det}(\mathbf{X}). \tag{1}$$

We will first describe the determinant part of the WF, moving then to the description of the JF used.

In TurboRVB, we use an atom-centered basis set of N_{orb} orbitals $\{\phi_{I,\nu}(\mathbf{r})\}$, where I and ν indicate the νth orbital centered on the Ith atom at the position $\mathbf{R}_I$. For this study, standard gaussian basis sets are chosen for the determinant, with orbital types

$$\phi_{I,\nu}(\mathbf{r}) = e^{-\frac{|\mathbf{r}-\mathbf{R}_I|^2}{Z_\nu}} Y_{l,m}^\nu, \tag{2}$$

where Z_ν is a numerical coefficient that describes how diffuse the atomic orbital is around the atom, while $Y_{l,m}^\nu$ is the spherical harmonic function relative to the orbital type of ν. For the sake of compactness, one can enumerate the basis as $\{\phi_\mu(\mathbf{r})\}$ combining the indices ν and I in a single index μ for a lighter notation. The use of a double zeta basis indicates that for the description of the 1s orbital of the hydrogen, we are using the s-wave and the p-wave orbitals, while for the triple zeta, we are also using d-wave orbitals.

In order to introduce the AGP WF, we first define a singlet wavefunction of an electron pair

$$\psi_2(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)f(\mathbf{r}_1, \mathbf{r}_2), \tag{3}$$

where f is the so called geminal function, which is assumed to be symmetric, namely, $f(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1)$, for a perfect singlet. The geminal function f is expanded as

$$f(\mathbf{r}_1, \mathbf{r}_2) = \sum_{k,l} \lambda_{k,l} \phi_k(\mathbf{r}_1) \phi_l(\mathbf{r}_2). \tag{4}$$

The generalization to a many electron WF requires an antisymmetrization of N/2 electron pairs of the form given in Eq. (3). The value of the WF for a given electronic configuration is given by the determinant of the matrix F

$$\langle x|AGP \rangle = \det F, \qquad (5)$$

where the $N/2 \times N/2$ matrix F is defined as $F_{i,j} = f(\mathbf{r}_i, \mathbf{r}_j)$, with the row index i corresponding to the up electrons and the column index j to the down ones. In the case in which $N_\uparrow \neq N_\downarrow$, we assume without loss of generality that $N_\uparrow > N_\downarrow$. If it is then necessary, we add $N_\uparrow - N_\downarrow$ columns to the matrix, corresponding to the unpaired orbitals written in the same basis set. Thus, the matrix is a $N_\uparrow \times N_\uparrow$ square matrix and its determinant can be evaluated, yielding also in this case the value of the AGP.

For our calculations, we often initialize the AGP or the SD WFs starting from a DFT calculation,[22] within the LDA approximation. Thus, it is important to translate without loss of information the SD into an AGP.

A SD is characterized by its set of MOs

$$\Phi_\alpha^{mol}(\mathbf{r}) = \sum_{i=1}^{N_{orb}} P_{\mu,\alpha} \phi_\mu(\mathbf{r}), \qquad (6)$$

which uniquely define it.

We can recast the SD into an AGP whose matrix F is diagonal in the basis of the MOs. The obtained geminal function can be written as

$$f(\mathbf{r}, \mathbf{r}') = \sum_\alpha \bar{\lambda}_{\alpha,\alpha} \Phi_\alpha^{mol}(\mathbf{r}) \Phi_\alpha^{mol}(\mathbf{r}'), \qquad (7)$$

where the diagonal form of the matrix $\bar{\lambda}$ is ensured by the orthogonality of the MOs. If we substitute the expression (6) into (7), we can have the description of the pairing function in the originally chosen basis set

$$\lambda = P_\uparrow \bar{\lambda} P_\downarrow^T. \qquad (8)$$

In this way, the SD is translated into an AGP of the same form given in Eq. (5), where the geminal functions have the same expression of Eq. (4) once the matrix (8) is substituted into Eq. (7). The SD written in this way appears as an AGP, but for each configuration **x**, the WF value is unchanged.

When we initialize the WF from a set of MOs, we have the same value for the AGP and the SD and the differences between the *Ansätze* can be seen only after the energy optimization. The AGP always provides an energy lower than the SD one, due to the larger variational freedom. Indeed, in the case of the SD, the matrix λ is constrained to have only $N/2$ orthogonal MOs,[25] corresponding therefore to a number of variational parameters much smaller than the one required for the AGP.

The two different WFs that we have introduced do not describe well the correlation between the electrons. Within QMC, it is easy to improve the quality of the WF, by multiplying the SD and the AGP with an exponential JF. This factor has also another important effect, as it speeds up the convergence to the CBS by improving the description of the atomic core, and thus not requiring large Z_ν values in the basis set. In particular, our JF is in the form

$$J(\mathbf{X}) = e^{U_{ei} + U_{ee}}, \qquad (9)$$

where U_{ei} is a single body term dealing explicitly with the electron-ion interaction and U_{ee} is a many-body term to take

into account the electronic correlation. The JF is particularly useful because, with an appropriate choice, it is possible to satisfy exactly the electron-electron and electron-ion cusp conditions of the many-body WF, a consequence of the Coulomb $1/r$ singularity at a short distance. The single body term is indeed written in the form

$$U_{ei} = \sum_{i=1}^{\#el} u_{ei}(\mathbf{r}_i), \qquad (10)$$

with u_{ei} being

$$u_{ei}(\mathbf{r}_i) = -\sum_{I=1}^{\#ions} Z_I \frac{1 - \exp(b_{ei}|\mathbf{r}_i - \mathbf{R}_I|)}{b_{ei}}, \qquad (11)$$

where Z_I is the atomic number of the atom I and b_{ei} is a variational parameter. The electron-electron term is written as

$$U_{ee} = \sum_{i<j} u_{ee}(\mathbf{r}_i, \mathbf{r}_j), \qquad (12)$$

where the sum is extended over the pairs of different electrons and where

$$u_{ee}(\mathbf{r}_i, \mathbf{r}_j) = \frac{|\mathbf{r}_i - \mathbf{r}_j|}{2(1 + b_{ee}|\mathbf{r}_i - \mathbf{r}_j|)} + \sum_{k,l} g_{k,l} \bar{\phi}_k(\mathbf{r}_i) \bar{\phi}_l(\mathbf{r}_j). \qquad (13)$$

The first term in Eq. (13) deals explicitly with the cusp conditions of the electron-electron potential with b_{ee} as variational parameter, and the second term instead takes explicitly into account the correlation via a pairing function in the same form of Eq. (4) with the matrix g as variational parameters. Here, the sum over k and l is extended over a basis set similar to the one used for the determinant, namely, determined by atomic-like wave functions of the form

$$\bar{\phi}_{J,\mu}(\mathbf{r}) = e^{-\frac{|\mathbf{r}-\mathbf{R}_J|}{Z_\mu}} Y_{l,m}^\mu, \qquad (14)$$

with μ denoting the orbital type and R_J denoting the nuclear positions of the atoms considered; as already done in Eq. (13), we combine μ and J in a single index.

The geometry of the system studied has a fixed bond distance along the y direction $r_y = 2.4$ a.u. This value gives the lowest energy result for the square geometry.[26] As sketched in Fig. 1, we study the system as a function of the distance r_x between the two vertical molecules.

For the optimization of the JAGP and JSD WFs, we used the same procedure. We consider two types of initializations that we denote in the following by OPT $r_x > r_y$ or OPT$r_x < r_y$, to indicate that the tetragonal symmetry is broken. In the first (second) case, we take $r_x = 4$ a.u. ($r_x = 1.8$ a.u.) and perform a DFT calculation for the initial Slater determinant, while the Jastrow is all zero but the initial one and two body parameters are set to a non-vanishing value $b_{ee} = 1/2$ and $b_{ei} = 1.3$. We initially optimize only the JF and we proceed with the full optimization of the AGP or SD with the JF. Then we move the atoms to a new position close to the original one maintaining the values of the variational parameters. If the new solution is reasonably close to the previous one, the stochastic optimization drives the WF to its new minimum. We
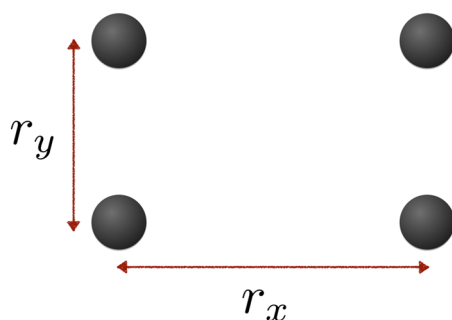
FIG. 1. Stylized picture of the system. While r_y is kept constant for all the calculations at a distance equal to 2.4 a.u., the distance r_x is varied for different system shapes.
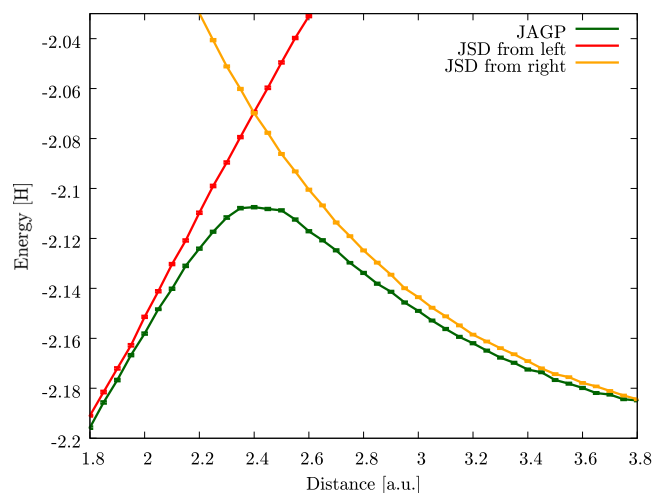

FIG. 2. Comparison between the variational energies of the different WFs. In orange, the energies of the JSD starting from the calculation at large r_x, in red, the ones starting from the small r_x, while in green, the JAGP variational energies are reported.

iterated this procedure to obtain the WFs at all the r_x distances for the JAGP and JSD. As we will discuss more extensively later, the JAGP optimization does not depend much on the starting WF, which is instead crucial for the JSD. In this latter case, the optimization procedure determines completely different results depending on the initial geometry, when we get close to the symmetric square case.

For the optimization of the AGP without the JF, we followed two different procedures yielding the same results. In one case, we started for every geometry from the corresponding optimized JAGP WF: we set the JF to 1 and we optimized the AGP from there. In the second case, we have used the same procedure adopted for the JAGP and JSD cases and obtained consistent energy values, validating the optimization procedure even in this difficult case without the Jastrow factor.

III. RESULTS AND DISCUSSION

The variational energies for the considered WFs are visible in Fig. 2 and reported in Table I. As shown in Fig. 2, the JSD values are reasonably accurate when the system is far from the square geometry, but very poor when $r_x \approx r_y$. We notice that for the JSD, the starting point is fundamental and the optimization result can significantly differ depending on the two different initializations. A particularly evident effect is the crossing of the JSD energy dispersions in Fig. 2. As expected, this problem does not affect the JAGP WF that shows the correct profile because close to the square geometry contains implicitly the two important Slater determinants with strong bonds either in the x or in the y direction. The optimizations of the JAGP both from OPT$r_x > r_y$ and OPT$r_x < r_y$ lead exactly to the same result. The qualitative difference between the two *Ansätze* is clearly shown in Fig. 3. The MOs try to localize the charge between two pairs of atoms to form two H_2 molecules. In particular, the JSD binds the atoms that are at smaller distances in the initial geometry: if we consider the OPT$r_x > r_y$ case, we obtain a higher charge density along the y direction, while if we start from the OPT$r_x < r_y$ case, a higher charge along the x direction shows up. The JAGP, instead, can resonate between these two configurations and catch the resonance valence bond

(RVB)[27] behaviour expected for the ground state of the square geometry.

The JAGP result is not only good at the variational level, but it provides also particularly accurate nodal surfaces for the DMC calculations. Indeed, as we can notice from Fig. 4 and from Table II, the DMC energies calculated using the nodes of the JAGP (cc-pVDZ) are lower than the ones calculated with the multi-determinant WF CAS(4,4), and FCI with the quadruple zeta basis.[1] This shows that even with a small basis set, the JAGP leads, in this controlled case, to almost optimal nodes and, by consequence, very accurate DMC energies. This is indeed remarkable, considering also that other more standard methods suffer not only for poor accuracy but also for the too large extension of the basis set. It also worth noticing that we obtain a higher gain in the region $r_x \approx r_y$ where the RVB picture is more relevant.

Thanks to the simplicity of the H_4 molecule, and the limited number of variational parameters involved in our WFs, we can use this model to study the genuine AGP without any JF. This case is particularly difficult with our stochastic optimization method because the statistical fluctuations of the energy are much larger. In principle, the AGP should be able to describe the static correlation of this molecule also without JF, with the two main contributions in the WF shown pictorially in Fig. 3(a). At the variational level, a much worse energy

TABLE I. Variational energies for different optimized WFs. The basis set used for the AGP and SD is indicated within parentheses. We show one point for each case: $r_x = r_y$, $r_x < r_y$, and $r_x > r_y$. All the energies are expressed in Hartree.

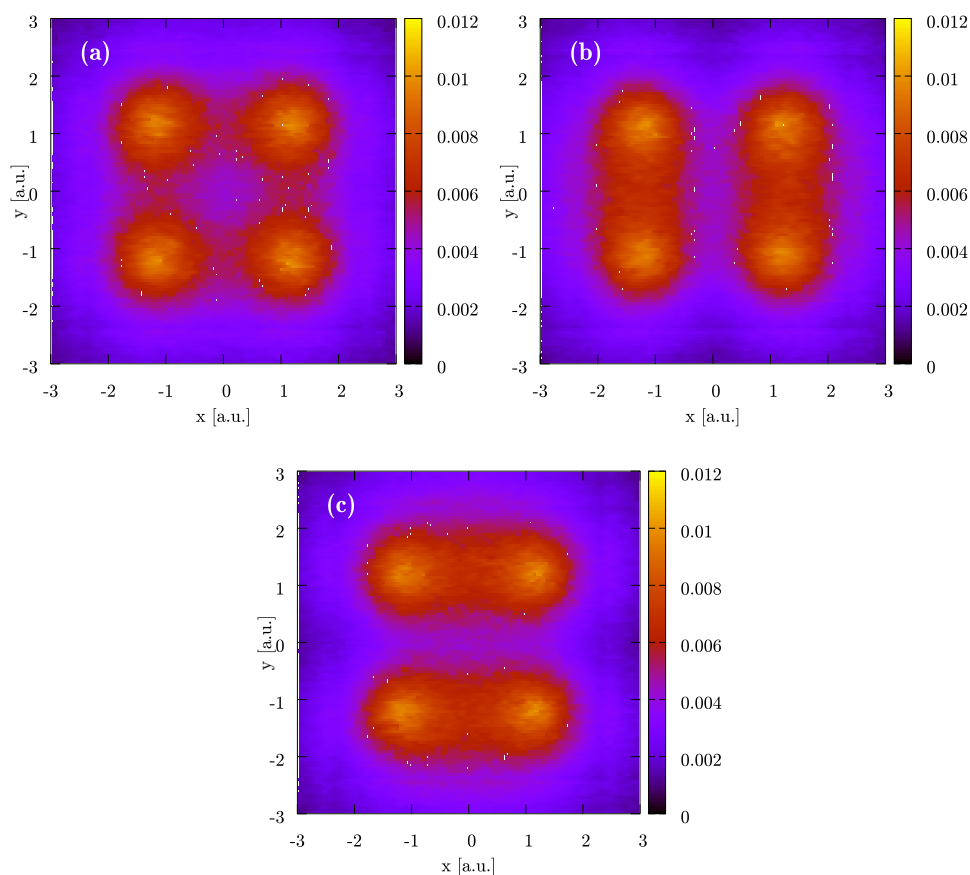| r_x	JSD (cc-pVDZ)	JAGP (cc-pVDZ)	JAGP (cc-pVTZ)
1.80	-2.1909 ± 0.0003	-2.1957 ± 0.0004	-2.1953 ± 0.0003
2.40	-2.0694 ± 0.0004	-2.1075 ± 0.0004	-2.1084 ± 0.0003
3.00	-2.1435 ± 0.0003	-2.1491 ± 0.0003	-2.1504 ± 0.0003

FIG. 3. Density plot on the *xy* plane of the systems for the square geometry for the JAGP and JS WFs. In panel (a), the density obtained with the JAGP WF, in panel (b), the density of the JSD optimized from $r_x > r_y$, while in panel (c), the one of the JSD from $r_x < r_y$.

for the AGP WF is expected because the correlation described by the JF is very important. However, it is very interesting to observe that the DMC results are significantly different with
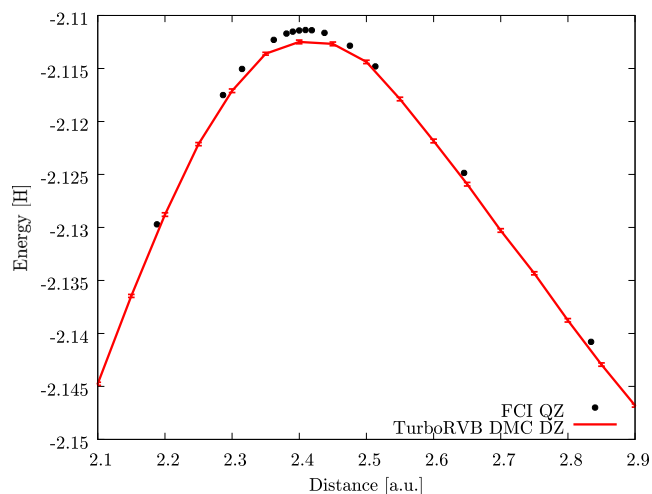

FIG. 4. Comparison between the DMC energy calculated using the node of the JAGP (cc-pVDZ) and the FCI (cc-pVQZ) calculation. On this scale, the error bars of the DMC calculation are not visible.

(JAGP) or without (AGP) JF, even considering that the JF > 0 cannot change the signs of the WF, and only the optimization of the AGP in the presence of the JF leads to a very accurate nodal surface. In Fig. 5(a), we can see that the variational energies of the AGP WF are indeed considerably higher compared to the JAGP ones. The smoothness of the curve and the reproducibility of the results indicate that the optimization is not stuck in spurious local minima. Instead the DMC results shown in Fig. 5(b) indicate an unphysical jump of the energy between two different phases. When $r_x \geq r_y$, the AGP is able to give very good energies that differ only few mH from the JAGP ones. Instead, when $r_x < r_y$, we can see a clear jump in the energy indicating that the nodal surface of the WF is not correctly described by the AGP. However, also in this regime, the nodes are still better than the ones provided by the JSD WF, with the energy values between the ones of the JSD and the JAGP.

TABLE II. Difference between the energies calculated with the DMC performed using the nodes of the JAGP, the ones of the CAS(4,4) and the FCI.[1] All the energies are expressed in Hartree.

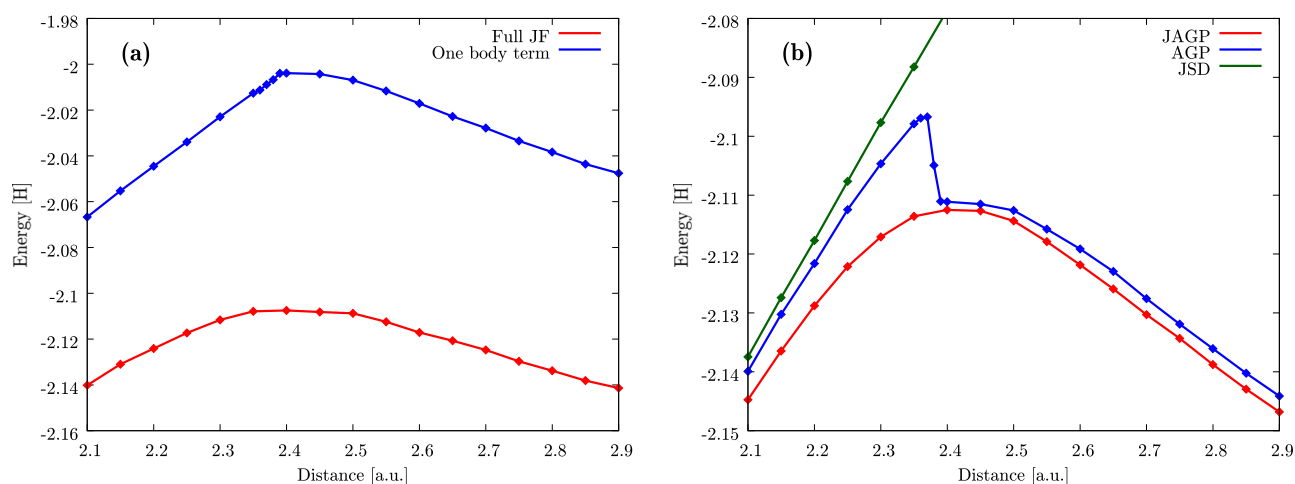| r_x	JAGP	CAS(4,4)	FCI
2.188	-2.1307 ± 0.0001	$-2.130\,33 \pm 0.000\,10$	-2.1297
2.400	-2.1125 ± 0.0002	$-2.111\,93 \pm 0.000\,05$	-2.1114
2.646	-2.1257 ± 0.0001	$-2.125\,58 \pm 0.000\,03$	-2.1248

FIG. 5. AGP and JAGP energies. In panel (a), we compare the values at the VMC level, while in panel (b), the corresponding DMC energies, within FNA, are shown.

In order to check that this transition was not due to some optimization error, we have calculated the WFs for $r_x < r_y$ starting from $r_x = r_y$, obtaining exactly the same Variational Monte Carlo (VMC) and DMC results. Qualitatively speaking, when the AGP is optimized in the presence of the JF, it can resonate between the correct configurations by avoiding double occupancies of singlet electron pairs,[27,28] which are energetically unfavorable. In some sense, the Jastrow correlation drives the optimization of the AGP toward the correct ground state energy and nodal surface.

Finally, as we can see from Table I, the JAGP is almost converged to the CBS limit with only the double zeta cc-pVDZ basis. The differences in energy with the cc-pVTZ are much below 1 mH/atom. This fast convergence is due to the term in Eq. (10) that fulfills the electron-ion cusp conditions and allows us to use a very small basis set to describe the system. In the AGP, the number of variational parameters scales with the square of the number of elements of the basis. It is therefore very important to reach a very accurate description with the smallest possible basis set. This can have a very dramatic impact for large systems where the dimension of the basis set is one of the most important bottlenecks of our JAGP calculations.

converged results in the CBS limit. Considering the above remarkable properties of our JAGP *Ansatz*, the extension to larger systems has been already employed in several cases, but its accuracy has not been deeply investigated. Thanks to the simplicity of this model system, we were also able to prove that the AGP alone, without the use of a JF, miserably fails, leading not only to inaccurate DMC energies but qualitatively wrong, as a discontinuity of the energy landscape as a function of the atomic positions was reported. In this case, the wrong nodal surface determined by the AGP for small r_x was not detectable at the VMC level because the optimized VMC energy was indeed a smooth and continuous function of r_x, as it should be from general grounds. This example leads us to conclude that the AGP optimization, in principle, possible with a very cheap and deterministic algorithm similar to the HF self-consistent method, is completely useless, as it can lead to spurious and qualitatively wrong results, in this sense much worse than simpler HF or DFT calculations. This work clearly indicates that instead the JAGP *Ansatz* opens the way to tackle even more complicated systems, when standard quantum chemistry methods are too much expensive and the single determinant approach does not work well.

IV. CONCLUSION

In this work, we have applied state of the art QMC techniques to a very simple system that has been used for benchmarking their accuracy in describing the strong electron correlations. We have shown that the use of the JAGP wave function is not only qualitatively correct but allows an almost exact description of the ground state with a computational effort similar to the widely used JSD, which miserably fails in this system, even within the more accurate DMC approach. We have also shown that the full optimization of our JAGP *Ansatz* guarantees a very fast convergence in the basis set so that no kind of extrapolation is necessary for almost

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