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# Chemical accuracy from quantum Monte Carlo for the benzene dimer

Sam Azadi<sup>1,a)</sup> and R. E. Cohen<sup>2</sup>

<sup>1</sup>Department of Earth Science and Thomas Young Centre, University College London, London WC1E 6BT, United Kingdom

<sup>2</sup>London Centre for Nanotechnology, University College London, London WC1E 6BT, United Kingdom and Extreme Materials Initiative, Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20015, USA

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We report an accurate study of interactions between benzene molecules using variational quantum Monte Carlo (VMC) and diffusion quantum Monte Carlo (DMC) methods. We compare these results with density functional theory using different van der Waals functionals. In our quantum Monte Carlo (QMC) calculations, we use accurate correlated trial wave functions including three-body Jastrow factors and backflow transformations. We consider two benzene molecules in the parallel displaced geometry, and find that by highly optimizing the wave function and introducing more dynamical correlation into the wave function, we compute the weak chemical binding energy between aromatic rings accurately. We find optimal VMC and DMC binding energies of  $-2.3(4)$  and  $-2.7(3)$  kcal/mol, respectively. The best estimate of the coupled-cluster theory through perturbative triplets/complete basis set limit is  $-2.65(2)$  kcal/mol [Miliordos *et al.*, J. Phys. Chem. A **118**, 7568 (2014)]. Our results indicate that QMC methods give chemical accuracy for weakly bound van der Waals molecular interactions, comparable to results from the best quantum chemistry methods. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4930137>]

## I. INTRODUCTION

Weak noncovalent van der Waals (vdW) interactions are fundamental to a wide range of topics relevant to physics, chemistry, and biology. A prototype vdW interaction is that resulting from the stacking between aromatic rings.<sup>1</sup> This interaction is crucially important in biological systems such as protein folding,<sup>2</sup> DNA's structure, and stability.<sup>3</sup> In addition, aromatic rings interactions play key roles in drug design,<sup>4</sup> electronics,<sup>5</sup> optical properties of materials,<sup>6</sup> polymer stability,<sup>7</sup> conjugated carbon networks,<sup>8</sup> and crystal growth processes.<sup>9,10</sup>

In general, vdW interactions are difficult to model accurately.<sup>11,12</sup> Local and semilocal density functionals are unable to describe the long-range electronic correlation energy which is the main part of the vdW forces. We use quantum Monte Carlo (QMC) and modern non-local exchange-correlation (XC) functionals. Previously empirical and semi-empirical corrections were used. For instance, one approach was to add empirical, pairwise atomic dispersion corrections of the form  $-C_6/R^6$ . To avoid double-counting electron correlation effects at short range, these contributions can be damped for small inter-atomic distances  $R$ . This method is referred to as density functional theory (DFT) plus dispersion (DFT-D) and has been applied on different systems using various XC functionals.<sup>13–18</sup>

Less empirical approaches were also developed. Effective nonlocal potentials were introduced,<sup>19</sup> where the parameters were determined using fitting to *ab initio* results. Becke and Johnson obtained dispersion coefficients  $C_6, C_8, C_{10}$  from

the multipole moments.<sup>20</sup> In their work, the moments were obtained from an electron and its exchange hole. The reliability of these approaches is similar to the DFT-D formalism.

Another density functional based method, widely applied on noncovalent systems, is the combination of DFT with symmetry-adapted perturbation theory, referred as DFT-SAPT or SAPT(DFT).<sup>21–24</sup> In these approaches, the dispersion term is obtained using the frequency dependent density susceptibility function of time dependent DFT (TD-DFT). The perturbation theory of intermolecular interactions can accurately predict the complete intermolecular potential energy surfaces for weakly bound molecular complexes.<sup>22</sup> From the point of view of perturbation theory, all the intermolecular interactions, including van der Waals interactions, contain four fundamental physical contributions: electrostatic, induction, dispersion, and exchange. The interactions differ only by proportions of these ingredients. The strongest of those interactions involve a larger negative contribution from the electrostatic forces as in hydrogen bonded systems. If the electrostatic contribution is small, like in interactions of rare gas atoms with molecules, the minima depths are often below 1 kcal/mol. Therefore, from this point of view, a system such as the benzene dimer is also a van der Waals complex.

Finally, by including nonlocal terms in DFT correlation energy functional, vdW-DFs<sup>25,26</sup> include the long range nonlocal correlation energy obtained by the plasmon pole approximation. These functionals were originally applied on different van der Waals systems to obtain potential energy curve (PEC).<sup>26</sup> DFT-vdW functionals result in significant improvements in equilibrium spacings between noncovalently bound complexes, as well as in binding energy of weak interacting systems. The efficiency and accuracy of different

<sup>a)</sup>s.azadi@ucl.ac.uk

DFT-vdW functionals on bulk systems were analyzed.<sup>27–29</sup> The functionals are a clear improvement over semi-local functionals, although tests on a wider range of systems are desirable.

Numerous theoretical works have compared different approximate quantum chemistry based methods for noncovalent weakly bound systems.<sup>30–33</sup> Particularly the coupled-cluster theory through perturbative triplets CCSD(T) which is often considered as the gold standard for chemical accuracy.<sup>34,35</sup> However, due to its substantial computational cost, scaling as  $N^7$  where  $N$  is the number of electrons, more efficient methods for vdW systems are highly desirable. These methods also cannot be applied to condensed matter. Thus, we consider QMC and compare with non-local density functionals.

Quantum Monte Carlo, which solves the electronic Schrödinger equation stochastically,<sup>36–39</sup> is an alternative approach to quantum mechanical methods. Diffusion quantum Monte Carlo (DMC) provides accurate energies for vdW systems.<sup>40–46</sup> DMC is also able to produce an accurate description of systems where many-body interactions play a key role.<sup>47,48</sup> In general, QMC based methods are faster than the most accurate post-Hartree-Fock schemes for large number of particles  $N$ . The computational cost of QMC methods scales usually as  $N^3$ - $N^4$  depending on the method.

The benzene dimer has become a benchmark system for electronic structure methods for systems where van der Waals interactions are important. Despite its simplicity, the problem of identifying the global minimum structure is particularly challenging as there are only subtle differences in the binding energies of the different configurations. According to quantum chemistry results, two critical factors for the binding energy of the benzene dimer are basis set and electron correlation.<sup>49</sup> Our previous comprehensive study of benzene molecules<sup>50</sup> illustrates the importance of basis set in QMC energy calculations. Once the Jastrow factor is optimized by keeping fixed the Slater determinant, we obtained a good description of the atomization energy of the benzene molecule only when the basis of atomic orbitals is large enough and close to the complete basis set (CBS) limit. In this work, we demonstrate that by using better trial wave functions and converged basis sets, we obtain a chemically accurate description of binding energy between aromatic rings.

## II. COMPUTATIONAL DETAILS

We used the CASINO QMC code<sup>51</sup> with a trial function of Slater-Jastrow (SJ) form,

$$\Psi_T(\mathbf{R}) = \exp[J(\mathbf{R})] \det[\psi_n(\mathbf{r}_i^\uparrow)] \det[\psi_n(\mathbf{r}_j^\downarrow)], \quad (1)$$

where  $\mathbf{R}$  is a  $3N$ -dimensional vector that defines the positions of all  $N$  electrons,  $\mathbf{r}_i^\uparrow$  is the position of the  $i$ 'th spin-up electron,  $\mathbf{r}_j^\downarrow$  is the position of the  $j$ 'th spin-down electron,  $\exp[J(\mathbf{R})]$  is the Jastrow factor, and  $\det[\psi_n(\mathbf{r}_i^\uparrow)]$  and  $\det[\psi_n(\mathbf{r}_j^\downarrow)]$  are Slater determinants of spin-up and spin-down one-electron orbitals. These orbitals were obtained from DFT calculations using the plane-wave-based Quantum Espresso code.<sup>52</sup> We used the local density approximation (LDA) to generate the orbitals

in the Slater determinant for the trial wave function. We chose a very large basis-set cutoff of 200 Ry to guarantee convergence to the complete basis set limit.<sup>50</sup> The plane-wave orbitals were transformed into a blip polynomial basis.<sup>53,54</sup> The quality of the blip expansion, meaning the fineness of the blip grid, can be improved by increasing the grid multiplicity parameter and consequently results in a greater number of blip coefficients. The value of this parameter in our work is 2.0. The LDA pseudopotentials are generated using the *OPIUM* pseudopotential generation program.<sup>55</sup> We also checked that the Kleinman-Bylander<sup>56</sup> transformation did not generate ghost states. In our DMC calculations, the pseudopotential energy was evaluated using a variational technique.<sup>57</sup> We used DMC time steps of 0.01 a.u. and 0.04 a.u. and extrapolated the results linearly to zero time step.

The Jastrow factor is a positive, symmetric, explicit function of interparticle distances. We used a Jastrow factor consisting of polynomial one-body (1B) electron-nucleus, two-body (2B) electron-electron, and isotropic three-body (3B) electron-electron-nucleus terms. The main approximation in fermionic QMC is the fixed node approximation. To reduce this error, we used backflow transformation (BF) in our trial wave functions.<sup>58</sup> In the backflow transformation, the orbitals in the Slater determinant are evaluated not at the actual electron positions, but quasi-electron positions that are functions of all the particle coordinates. The backflow function, which describes the offset of the quasi-electron coordinates relative to the actual coordinates, contains free parameters to be determined by an optimization method. It allows the nodal surfaces to move within variational optimization, so with BF, the QMC is no longer strictly fixed node. However, the subsequent DMC computations use the nodal surface that was determined during the variational quantum Monte Carlo (VMC) step.

In QMC calculations, correlated wave function can be obtained by replacing the single determinant by a sum over configuration state functions (CSFs), using BF transformations of the electronic coordinates or by using pairing wave functions.<sup>59–63</sup> Our BF transformation includes both electron-electron and electron-proton terms, given by

$$X_i(\{\mathbf{r}_j\}) = \mathbf{r}_i + \xi_i^{(e-e)}(\{\mathbf{r}_j\}) + \xi_i^{(e-P)}(\{\mathbf{r}_j\}), \quad (2)$$

where  $X_i(\{\mathbf{r}_j\})$  is the coordinate of electron  $i$  which depends on the configuration of the system  $\{\mathbf{r}_j\}$ ,  $\xi_i^{(e-e)}(\{\mathbf{r}_j\})$  and  $\xi_i^{(e-P)}(\{\mathbf{r}_j\})$  are electron-electron and electron-proton backflow displacements of electron  $i$ , respectively, given by

$$\xi_i^{(e-e)}(\{\mathbf{r}_j\}) = \sum_{j \neq i}^{N_e} \alpha_{ij}(r_{ij}) \mathbf{r}_{ij}, \quad (3)$$

$$\xi_i^{(e-P)}(\{\mathbf{r}_j\}) = \sum_I^{N_P} \beta_{iI}(r_{iI}) \mathbf{r}_{iI}, \quad (4)$$

where  $\alpha_{ij}(r_{ij})$  and  $\beta_{iI}(r_{iI})$  are polynomial functions of electron-electron and electron-proton distance, respectively, containing optimizable parameters.

We use two methods for wave function optimization: variance minimization and energy minimization.<sup>64,65</sup> The parameters of Jastrow and backflow are first optimized

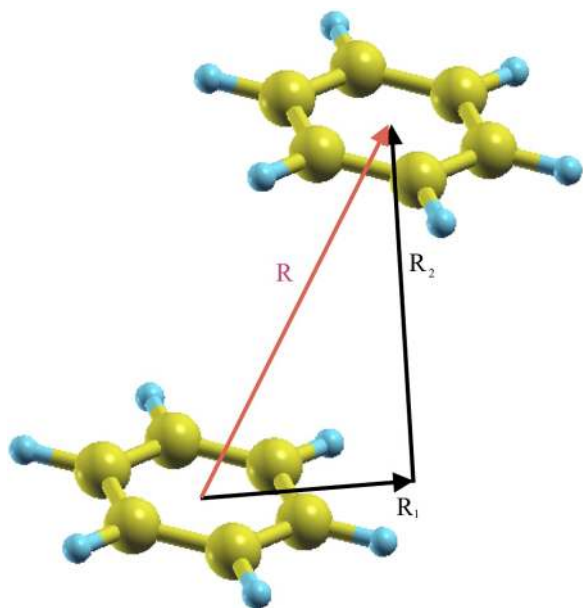


FIG. 1. Parallel-displacement (PD) geometry of benzene dimer ( $C_{2h}$  symmetry) studied in this work.  $R$  indicates the distance between centers  $R = \sqrt{(R_1^2 + R_2^2)}$ . In our study, centers displacement  $R_1 = 1.6 \text{ \AA}$  is fixed.

by variance minimization at the variational Monte Carlo level.<sup>66–70</sup> Since trial wave functions generally cannot exactly represent an eigenstate, the energy and variance minima do not coincide. Therefore, energy minimization should produce lower VMC energies. We have found that the lower VMC energies lead to lower DMC energies if we use backflow transformations. This is due to improved many-body nodes as well as reduction in the errors induced by using non-local pseudopotentials.

We used the Quantum Espresso code<sup>52</sup> for DFT-vdW calculations with ultrasoft pseudopotentials<sup>71</sup> and Perdew-Burke-Ernzerhof (PBE)<sup>72</sup> exchange correlation functionals. The plane wave basis had a well-converged cutoff of 80 Ry.

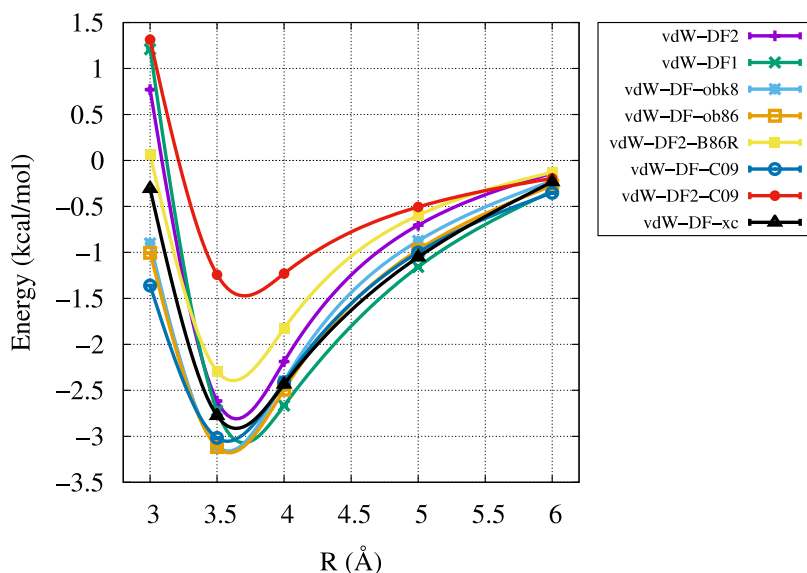


FIG. 2. DFT energy of PD benzene dimer as a function of their separation obtained using different vdW-DF functionals. The reference is chosen at  $R = 10 \text{ \AA}$ . Using polynomial fitting (Appendix), the optimal DFT binding energies obtained by vdW-DF1,<sup>25</sup> vdW-DF2,<sup>26</sup> vdW-DF-obk8, vdW-DF-ob86, vdW-DF2-B86R,<sup>28,29</sup> vdW-DF-C09, vdW-DF2-C09,<sup>82</sup> and vdW-DF-cx<sup>83</sup> are  $-3.1$ ,  $-2.8$ ,  $-3.1$ ,  $-3.2$ ,  $-2.4$ ,  $-3.0$ ,  $-1.5$ , and  $-2.9$  kcal/mol at  $R = 3.7$ ,  $3.65$ ,  $3.58$ ,  $3.60$ ,  $3.63$ ,  $3.57$ ,  $3.71$ , and  $3.65 \text{ \AA}$ , respectively. The experimental binding energy is  $-2.4(4)$  kcal/mol.<sup>88</sup>

### III. RESULTS AND DISCUSSION

We used the experimental geometry for the benzene molecule, where the C–C and C–H bond lengths are 1.39 and 1.09 Å, respectively. Experiments support the existence of these three benzene dimer configurations,<sup>73</sup> the parallel (sandwich), the T-shaped ( $C_{2v}$ ), and the slipped-parallel or parallel-displacement (PD,  $C_{2h}$ )<sup>74</sup> configurations. The T-shaped, where two benzene molecules are perpendicular to each other, and the PD configurations are more energetically favored than the parallel sandwich geometry.<sup>75–81</sup> T-shaped and PD configurations of benzene dimer are almost isoenergetic, and the benzene dimer potential energy surface is quite flat with several local minima separated by tiny barriers. In this work, we focus on the PD configuration as shown in Figure 1. Centers of two parallel benzene rings are displaced by  $R_1 = 1.6 \text{ \AA}$  and is fixed in our calculations.

Figure 2 illustrates DFT potential energy curve obtained using different vdW functionals. We use vdW-DF1,<sup>25</sup> vdW-DF2,<sup>26</sup> vdW-DF-obk8, vdW-DF-ob86, vdW-DF2-B86R,<sup>28,29</sup> vdW-DF-C09, vdW-DF2-C09,<sup>82</sup> and vdW-DF-cx<sup>83</sup> functionals. All vdW functionals use Slater exchange and PW<sup>84</sup> correlation functionals. The non-local terms are either vdW-DF1 or vdW-DF2. Employing various gradient correction on exchange energy is the main difference between these functionals. Using polynomial fitting (Appendix), the optimal DFT binding energies obtained by vdW-DF1, vdW-DF2, vdW-DF-obk8, vdW-DF-ob86, vdW-DF2-B86R, vdW-DF-C09, vdW-DF2-C09, and vdW-DF-cx are  $-3.1$ ,  $-2.8$ ,  $-3.1$ ,  $-3.2$ ,  $-2.4$ ,  $-3.0$ ,  $-1.5$ , and  $-2.9$  kcal/mol at  $R = 3.7$ ,  $3.65$ ,  $3.58$ ,  $3.60$ ,  $3.63$ ,  $3.57$ ,  $3.71$ , and  $3.65 \text{ \AA}$ , respectively. Free-energy landscape calculations using Car-Parrinello molecular meta-dynamics methods using the BLYP density functional with dispersion corrections predict that T-shape geometry is more stable at all temperatures.<sup>85</sup> However, the PD configuration with  $C_{2h}$  symmetry has been determined using optical absorption spectroscopy, whereas a polar V-shape configuration with  $C_{2v}$  symmetry has been suggested by multiphoton ionization mass spectroscopy.<sup>86,87</sup>

TABLE I. QMC energies (kcal/mol) of the PD benzene dimer obtained by VMC and DMC using one-body (1B), two-body (2B), three-body (3B) Jastrow factors and Backflow (BF) transformations. Energies are calculated at different distance geometry  $R$  Å. Energy differences are calculated with respect to the large  $R = 10$  Å. Experimental binding energy is  $-2.4(4)$  kcal/mol.<sup>88</sup>

R	VMC	DMC	VMC	DMC	VMC	DMC
	1B+2B	1B+2B	1B+2B+3B	1B+2B+3B	1B+2B+3B+BF	1B+2B+3B+BF
3.0	7.23(9)	5.63(9)	6.9(2)	5.3(1)	5.0(2)	4.4(3)
3.5	2.50(9)	-0.81(9)	0.0(2)	-0.9(1)	-1.2(2)	-1.8(2)
4.0	0.55(9)	-1.45(9)	-0.6(2)	-1.5(1)	-2.2(2)	-2.5(2)
5.0	0.02(9)	-0.71(8)	-0.0(2)	-0.8(1)	-0.6(2)	-1.1(2)
6.0	0.00(9)	-0.31(9)	0.0(2)	-0.4(2)	-0.3(3)	-0.4(2)

Table I lists QMC energies of benzene dimer in the PD configuration obtained by VMC and DMC methods at different separation distance  $R$ . Lowest VMC and DMC energies are obtained at  $R = 4.0$  Å. Adding 3B-Jastrow factor substantially improves the VMC energies. The 3B-Jastrow function takes care of what is missing in the 1B and 2B Jastrow factors, meaning, the explicit dependence of the electron correlation on the ionic positions. At  $R = 4.0$  Å, the difference between VMC energies obtained with and without 3B-Jastrow factor is about  $-1.1(2)$  kcal/mol, whereas in DMC, the difference is negligible. However, BF transformations significantly lower the QMC energies. At  $R = 4.0$  Å, BF transformations lower the energies by  $-1.6$  and  $-1.0$  kcal/mol at VMC and DMC calculations, respectively. Adding 3B-Jastrow factor and BF transformations improves the VMC and DMC energies by about  $-2.7(2)$  and  $-1.0(2)$  kcal/mol, respectively.

The VMC energies obtained with BF are lower than DMC energies without BF. This indicates that VMC with BF could be a useful level of theory to describe nonlocal long term interactions. In general, VMC calculations are significantly less expensive than DMC ones. Also, VMC has advantages for calculating expectation values of quantities more than the energy. Our QMC results clearly demonstrate that increasing the complexity of the wave function by including the BF

correlations and 3B-Jastrow terms plays key role in accurate describing of vdW interactions.

Figure 3 illustrates QMC potential energy curve of benzene dimer as a function of their distance obtained by VMC and DMC calculations. Using polynomial fitting (Appendix), the optimal values of binding energies at VMC level obtained by 1B+2B+3B-Jastrow and 1B+2B+3B-Jastrow plus BF correlations are  $-0.9(2)$  and  $-2.3(4)$  kcal/mol, respectively. DMC optimal values obtained by 1B+2B-Jastrow, 1B+2B+3B-Jastrow, and 1B+2B+3B-Jastrow plus BF are  $-1.7(2)$ ,  $-1.8(2)$ , and  $-2.7(3)$  kcal/mol, respectively. Using only 1B+2B-Jastrow factor, VMC is unable to provide a bound benzene dimer. Using the same Jastrow factor, the DMC binding energy is close to those ones obtained by SOS-MP2 method.<sup>49</sup> Employing 3B-Jastrow factor significantly improves the VMC binding energy, whereas it does not lower the DMC binding energy considerably. At the variational level, the inclusion of a 3B-Jastrow term provides additional dynamical correlation into the wave function and it is essentially useful for studying nonlocal vdW interactions.

Although a 3B-Jastrow factor improves the binding energy of benzene dimer in VMC, substantial enhancement is obtained by employing BF correlations. The optimal values indicate that VMC and DMC energies are improved by  $-1.4$  and  $-0.9$  kcal/mol, respectively. It suggests that BF is effective at improving the nodal surface of benzene dimer in PD geometry. Considering that the LDA wave function often has too many nodal pockets, it is conceivable that BF coordinate transformations could modify the number of nodal pockets of a wave function.

Table II shows the binding energy of benzene dimer in PD geometry obtained by different methods. Since the benzene dimer is a standard test for high-level quantum chemistry methods for proper characterization of vdW interactions, there are many more results; a comprehensive comparison between different high-level *ab initio* approaches is reported recently.<sup>33</sup> They provide databases for noncovalent interactions. 49 bimolecular complexes in 345 geometry configurations are partitioned into subsets based on bonding motif. Benzene dimer is in the dispersion-dominated subset. Our DMC result is close to CCSD(T) (Table II), which is considered the gold standard for chemical accuracy. The CBS limit can now be estimated more precisely in the CCSD(T) framework. Our VMC results is comparable with those ones obtained by lattice regularized diffusion Monte Carlo (LRDMC) method using Jastrow-AGP (antisymmetrized geminal power) wave function.<sup>44</sup> The

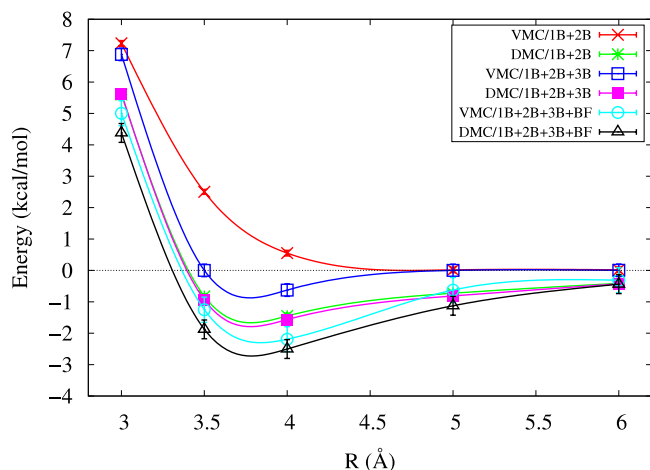


FIG. 3. QMC energy of benzene dimer as a function of their distance obtained using VMC and DMC methods. Energy differences are calculated with respect to the large  $R = 10$  Å. Using polynomial fitting (Appendix), the optimal values of binding energies obtained by DMC/1B+2B, VMC/1B+2B+3B, DMC/1B+2B+3B, VMC/1B+2B+3B+BF, and DMC/1B+2B+3B+BF are  $-1.7(2)$ ,  $-0.9(2)$ ,  $-1.8(2)$ ,  $-2.3(4)$ , and  $-2.7(3)$ , respectively.

TABLE II. Binding energies  $E_b$  of the PD benzene dimer obtained at different level of theories. The zero point vibrational energy is not included.

Method basis set	R (Å)	$E_b$ (kcal/mol)	References
VMC/1B+2B+3B+BF	3.9(3)	-2.3(4)	This work
DMC/1B+2B+3B+BF	3.8(3)	-2.7(3)	This work
DFT-D/BLYP  TZVP	3.486	-2.88	89
vdW-DF2	3.65	-2.8	This work
vdW-DF1	3.7	-3.1	This work
vdW-DF-obk8	3.58	-3.1	This work
vdW-DF-ob86	3.60	-3.2	This work
vdW-DF2-B86R	3.63	-2.4	This work
vdW-DF-C09	3.57	-3.0	This work
vdW-DF2-C09	3.71	-1.5	This work
vdW-DFT-cx	3.65	-2.9	This work
CCSD(T) CBS	3.9	-2.65(2)	49
CCSD(T) CBS( $\Delta$ aDZ)	N/A	-2.73	32
MP2 CBS	3.66	-5.00(1)	49
JAGP-LRDMC	4.1(2)	-2.2(3)	44
FNDMC	N/A	-1.65(42)	45
Experiment	N/A	-2.4(4)	88
Experiment	N/A	-1.6(2)	90

correlated AGP<sup>62</sup> is the particle number conserving version of the Bardeen-Cooper-Schrieffer (BCS) wave function. A singlet valence bond between two electrons of opposite spin is determined by a geminal function. This framework successfully applied to identify the Kekulé and Dewar contributions to the chemical bond of the benzene molecule.<sup>63</sup>

The T-shape configuration was studied before using QMC methods.<sup>46</sup> Using 1B, 2B, and 3B Jastrow factors, they found that the binding energy of T-shape configuration obtained by fixed-node (FN)-DMC is  $-2.88(16)$  kcal/mol. An accurate study of noncovalent systems illustrates the importance of Jastrow factor optimization in obtaining reliable results.<sup>45</sup> They investigated in detail all technical parameters of QMC simulations. They also have found that the binding energies for T-shape and PD configurations are  $-3.77(39)$  and  $-1.65(42)$  kcal/mol, respectively. The CCSD(T) estimates of T-shape binding energy is  $-2.74$  kcal/mol.<sup>45</sup> By considering the reduction of the binding energy due to the ZPE ( $\Delta$ ZPE = 0.37 kcal/mol),<sup>44</sup> our DMC energy obtained by 3B-Jastrow and BF correlations is in excellent agreement with experiment.<sup>88</sup> Among DFT results obtained by different vdW functionals, vdW-DF2-B86R energy is close to our VMC/1B+2B+3B+BF result. vdW-DFT-cx and vdW-DF2

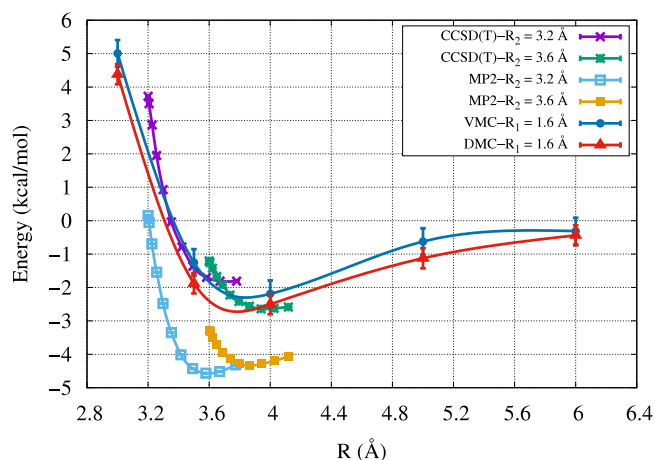


FIG. 4. Energy for PD benzene dimer as function of their centers distance obtained by different methods. We only compare our VMC/1B+2B+3B+BF (VMC), DMC/1B+2B+3B+BF (DMC) results. The MP2 and CCSD(T) data were taken from Ref. 92.

energies are close to our DMC/1B+2B+3B+BF energy.

We found that the dependence of the DMC energies on the quality of the trial wave function is significant. Whereas the Jastrow factors keep electrons away from each other and essentially improve the trial wave function, they do not change the nodal surfaces. It has been argued that BF transformation and 3B Jastrow correlation arises as the next-order improvements to the standard Slater-Jastrow wave function.<sup>91</sup> As our results show, the importance of BF correlations within DMC calculations is that they alter the nodal surface and can therefore be used to reduce the FN error. However, more complexity of BF-WF comparing to SJ-WF causes additional computational cost in QMC calculations. One of the most expensive operations in QMC calculations is the evaluation of the orbitals and their first two derivatives. The evaluation of the collective coordinates in BF-WF introduces significantly more computational cost. Moreover, whereas QMC calculations with SJ-WF require only the value, gradient, and Laplacian of each orbital  $\psi$ , BF calculations also require cross derivatives such as  $\partial^2\psi/\partial x\partial y$ . The most important complicating factor arising from BF transformations is that they make each orbital in the Slater determinants depend on the coordinates of every particle.

Figure 4 illustrates the potential energy curves for PD benzene dimer as function of ring centers distance at different level of theory. CCSD(T) and MP2 results were calculated

TABLE III. Piecewise polynomial fitting parameters for QMC results. Smoothing parameter  $\alpha$ , the sum of squares due to error (SSE), R-square, Root Mean Squared Error (RMSE), and optimal parameters ( $opt$ ) for each method. Energies  $E$  and distance geometry  $R$  are in kcal/mol and Å, respectively.

	VMC 1B+2B	DMC 1B+2B	VMC 1B+2B+3B	DMC 1B+2B+3B	VMC 1B+2B+3B+BF	DMC 1B+2B+3B+BF
$\alpha$	0.998 971 6	0.999 915 5	0.999 915 5	0.999 915 5	0.999 860 7	0.999 860 7
SSE	0.003 72	0.000 222 3	0.000 263 8	0.000 234 5	0.000 398 8	0.000 513 9
R-square	0.999 9	1.000 0	1.000 0	1.000 0	1.000 0	1.000 0
RMSE	0.169 4	0.137 9	0.150 2	0.141 6	0.144 3	0.163 8
$E_{opt}$	0.00	-1.66	-0.87	-1.77	-2.31	-2.71
$R_{opt}$	4.50	3.78	3.78	3.80	3.85	3.79

TABLE IV. Piecewise polynomial fitting parameters for DFT results. Smoothing parameter  $\alpha$ , the sum of squares due to error (SSE), R-square, Root Mean Squared Error (RMSE), and optimal parameters ( $opt$ ) for each method. Energies  $E$  and distance geometry  $R$  are in kcal/mol and Å, respectively.

	vdW-DF-obk8	vdW-DF-ob86	vdW-DF2-B86R	vdW-DF-C09	vdW-DF2-C09	vdW-DF-cx	vdW-DF1	vdW-DF2
$\alpha$	0.999 621 4	0.999 621 4	0.999 621 4	0.999 621 4	0.999 621 4	0.999 770 3	0.999 770 35	0.999 770 35
SSE	0.001 203	0.001 034	0.001 1	0.000 706 8	0.000 841 1	0.000 385 3	0.000 731 8	0.000 743 9
R-square	0.999 8	0.999 8	0.999 7	0.999 8	0.999 8	0.999 9	0.999 9	0.999 9
RMSE	0.153 9	0.142 6	0.147 1	0.117 9	0.128 6	0.111	0.152 9	0.154 2
$E_{opt}$	-3.13	-3.16	-2.37	-3.03	-1.46	-2.90	-3.06	-2.79
$R_{opt}$	3.58	3.60	3.63	3.57	3.71	3.65	3.71	3.65

using aug-cc-pVQZ\* (=aug-cc-pVQZ-g function on carbon-function on hydrogen) basis set.<sup>92</sup> At the MP2 level, the equilibrium distances between aromatic rings are  $R_1 = 1.6$  and  $R_2 = 3.4$  Å. At the CCSD(T) level, they are  $R_1 = 1.6$  and  $R_2 = 3.6$  Å. MP2 calculations produce over-binding. Comparing to T-shaped benzene dimer configuration, which we have not studied in this work, it has been claimed that PD configuration has larger electrostatic interactions,<sup>92</sup> since the positive hydrogens on each aromatic ring are located on top of the negative carbons of the other ring. In the PD geometry, two benzene rings are closer together than in either the sandwich or the T-shaped configurations. Therefore, the incursion of the electronic orbitals of each ring makes the electrostatic interaction more stable.

#### IV. CONCLUSION

We find that QMC can give chemical accuracy for the benzene dimer. The good agreement among our results, experiments and quantum chemistry methods, is an important sign of the capability of the QMC based methods to provide accurate description of very weak intermolecular interactions based on vdW dispersive forces. We find that adding 3B-Jastrow terms and BF transformations leads to significant improvement in the accuracy of the weak vdW interaction between aromatic rings. BF-VMC energies are significantly lower than SJ-VMC and therefore BF-VMC could be useful alternative for a SJ-DMC calculations, which are more expensive. The accuracy of our VMC results compared with DMC is evidence of the high accuracy of our trial wave function. BF correlations give substantial enhancement in trial wave function of aromatic rings. By improving the nodal surface of wave function, it leads to a significant reduction in binding energy between two benzene molecules. Improved trial wave functions will be useful in VMC calculations of quantities other than the energy, which are usually more difficult to obtain accurately than the energy. We used single determinant wave functions in this work, but BF can also be combined with other types of wave functions such as multideterminant or pairing wave functions.

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#### APPENDIX: ENERGY CURVE FITTING FUNCTIONS

In this appendix, we report fitting parameters. We used piecewise polynomial fitting functions. Tables III and IV list fitting parameters including smoothing parameter  $\alpha$ , the sum of squares due to error (SSE), R-square, Root Mean Squared Error (RMSE), and optimal parameters ( $opt$ ) for each method.

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