

Resonating valence bond pairing energy in graphene by quantum Monte Carlo

S. Azadi^{1,*}, A. Principi¹, T. D. Kühne^{2,3,4} and M. S. Bahrany¹¹*Department of Physics and Astronomy, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom*²*Center for Advanced Systems Understanding, Untermarkt 20, D-02826 Görlitz, Germany*³*Helmholtz Zentrum Dresden-Rossendorf, Bautzner Landstraße 400, D-01328 Dresden, Germany*⁴*TU Dresden, Institute of Artificial Intelligence, Chair of Computational System Sciences, Nöthnitzer Straße 46, D-01187 Dresden, Germany*

(Received 23 October 2025; revised 12 December 2025; accepted 13 February 2026; published 2 March 2026)

Whether short-range electron pairing can be stabilized in graphene remains a central question because pristine graphene is a semimetal with vanishing density of states at the Dirac point. We show that geometry alone can enhance short-range pairing correlations in confined graphene. Using real-space quantum Monte Carlo with correlated trial wavefunctions, we control a simple geometric knob, the commensurability of the simulation cell with the Dirac points, which creates or removes a small, single-particle gap in finite graphene samples. Diffusion quantum Monte Carlo reveals a clear dichotomy, when this geometry-induced gap is present, a resonance-valence-bond(RVB)-like state is energetically favored. Whereas when the spectrum is gapless and cell includes the Dirac points, no RVB energy gain is found. The effect persists in large cells at fixed geometry, establishing that confinement and commensurability can tip the energetic balance toward singlet pairing, while pristine bulk graphene shows no intrinsic RVB instability. These results identify a practical, geometry-controlled route to amplify pairing tendencies in nanoscale graphene devices and provide many-body benchmarks for interpreting finite-cell *ab initio* calculations. Our results also suggest design principles, via shape, aspect ratio, or mild superlattice modulations, to engineer stronger electronic correlations in carbon-based nanoelectronics.

DOI: [10.1103/hmmc-nhdl](https://doi.org/10.1103/hmmc-nhdl)

Many-body electron correlations in pristine graphene [1–4] are central to its most distinctive two-dimensional (2D) properties. The long-range Coulomb interaction is only marginally screened, leading to logarithmic renormalization of the Dirac Fermi velocity, breaking down the Fermi liquid picture, reduced quasiparticle weight, and scale-dependent effective coupling [5–7]. The electrons near the Fermi level follow the Lorentz invariant theory, where the kinetic energy is a linear function of the momentum given by $K = v_F |\mathbf{p}|$ [3] where v_F is the Fermi-Dirac velocity and the property of a material. This linear behavior has a profound effect that causes the ratio of Coulomb to kinetic energy α to become independent of the electronic density, $\alpha \propto 1/\epsilon v_F$ where ϵ is also a material property. This is opposite to the Fermi liquid where the density parameter r_s represents the weakly or strongly correlated regimes when it is small or large, respectively [8,9]. Since the electronic density of states vanishes at the Dirac point, graphene is not a metal, but at the same time it is not an insulator either because it does not have a gap in the spectrum [10–15]. From an electron correlation point of view, the presence of the Dirac point makes the graphene a unique system. Another outcome of $K \propto p$ in graphene compared to

most systems with $K \propto p^2$ is related to the quantization of energy in confined electrons [16]. If $K \propto p^2$, the quantized energy levels of electrons, which are confined to an area of size a , are proportional to space as $\Delta\epsilon_0 \propto 1/a^2$, where as in graphene due to $K \propto p$, $\Delta\epsilon \propto 1/a$. Hence, the size dependence of single particle energy states, which are described by plane waves and energy bands in periodic systems and determined by integration over the Brillouin zone, in small graphene sample size is different from those in the infinite system size limit. Hence, in a nanoscale system size, crystal momentum is not a good quantum number, causing the bands touching at the Dirac point to become discrete levels. Also, since the Coulomb energy scales as $1/a$, the Coulomb effects are stronger in nanoscale graphene samples. Taken together, these unconventional behaviors imply that correlation-driven phenomena in graphene such as spin-liquid state [17,18], superconductivity [5], and electron pairing in general, are size dependent. Controlling electronic correlations in graphene based systems typically relies on doping, strain, and band-structure engineering such as flat bands [7,11,19–21]. Here we highlight a simpler and broadly applicable lever which is geometry. This work focuses on geometry-controlled amplification of electronic correlations in graphene by using the resonating valence bond (RVB) based pairing energy as an operational metric. Our results demonstrate that confinement and commensurability can enhance short-range electronic correlations in graphene purely through geometry, without invoking intrinsic mass terms, phonons, or flat bands.

The RVB theory [22–25] was originally proposed by Pauling to describe the electronic structure of aromatic

*Contact author: sam.azadi@manchester.ac.uk

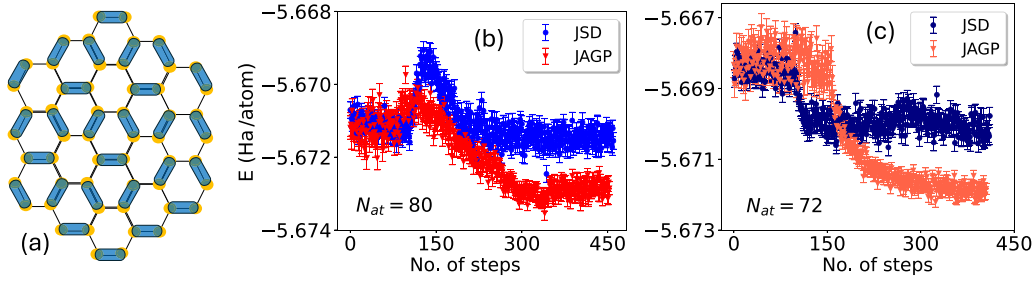


FIG. 1. (a) A spin-singlet dimer configuration (blue color) on graphene lattice. The resonating valence bond (RVB) state is composed of a superposition of such configurations. Three sp^2 orbitals form the σ band containing three localized electrons, while the bonding among the p_z orbitals of different lattice sites generate a valence band (π band) having one electron. The antibonding configuration generates the conduction π^* band. VMC energy as a function of the number of optimization steps computed using JSD and JAGP wave functions for finite-gap system with number of atoms in simulation cell $N_{at} = 80$ (b) and zero-gap system with $N_{at} = 72$ (c).

molecules [24]. Within this framework, the bonding in graphene arises from a superposition of multiple valence bond configurations, reflecting the delocalized nature of its π electrons (Fig. 1). Anderson applied the RVB concept to construct a nondegenerate ground state for a spin-half antiferromagnetic configuration on a triangular lattice [22,26]. A valence bond is defined as a spin-singlet state given by $(S_i, S_j) = (|S_{\uparrow i} S_{\downarrow j}\rangle - |S_{\downarrow i} S_{\uparrow j}\rangle)/\sqrt{2}$. An RVB state is a tensor product of the valence bond states:

$$|\Phi_{\text{RVB}}\rangle = \sum_{i_1 j_1 \dots i_n j_n} \alpha_{(i_1 j_1 \dots i_n j_n)} |(S_{i_1}, S_{j_1}) \dots (S_{i_n}, S_{j_n})\rangle, \quad (1)$$

where $(S_{i_1}, S_{j_1}) \dots (S_{i_n}, S_{j_n})$ are singlet configurations over the lattice, and $\alpha_{(i_1 j_1 \dots i_n j_n)}$ are variational parameters obtained by minimization of the ground state energy of a given Hamiltonian. The many-body wave function (WF) of the system is a summation over all possible configurations of dividing the lattice into dimers. The number of $\alpha_{(i_1 j_1 \dots i_n j_n)}$ variational parameters is considerably large, causing difficulties for practical application of the above RVB WF. Noting that the Bardeen-Cooper-Schrieffer (BCS) conventional superconducting state is formed of spin-singlet Cooper pairs of electrons with opposite momentum, it was suggested that a practical RVB WF can be formed from BCS WF using a Gutzwiller projection P_{∞} , $|\Phi_{\text{RVB}}\rangle = P_{\infty} |\Psi_{\text{BCS}}\rangle$, in which $P_{\infty} = \prod_i (n_{i,\uparrow} - n_{i,\downarrow})^2$, with n_i denotes the particle density on site i , and $|\Psi_{\text{BCS}}\rangle = \exp(\sum_{i,j} f_{i,j} c_{i,\uparrow}^\dagger c_{j,\downarrow}^\dagger) |0\rangle$ where the pairing function in real space $f_{i,j} = f_{j,i}$ depends on relative distance $\mathbf{R}_i - \mathbf{R}_j$. In fact, P_{∞} eliminates all WF components with doubly occupied sites from the BCS WF and constrains the charge degrees of freedom. Therefore, the RVB WF is insulating with no density fluctuations. For a disordered antiferromagnetic system, it was suggested that the valence bond dimers in the RVB WF are dominated by short range pairs [22], meaning $f_{i,j} \neq 0$ only for nearest-neighbor (NN) sites, which results in a spin-liquid state without long-range spin order [27].

Quantum Monte Carlo calculations of correlated electrons on a graphene lattice predict a short-ranged RVB quantum spin-liquid state, which proposes the possibility of unconventional superconductivity via doping with $d + id$ pairing symmetry [17,18,20]. The stability of a spin-liquid state in the Hubbard model on the graphene lattice close to an

antiferromagnetic Mott insulator [17] could be similar to some organic antiferromagnet with a possible spin-liquid ground state [28,29]. The application of RVB theory is not limited to the strongly correlated regime near the Mott transition or the spin-liquid model, but it can be expanded to describe the electronic structure and pairing mechanism in strongly correlated real systems [30,31].

In this work, we investigate RVB correlations in monolayer graphene using real-space variational and diffusion quantum Monte Carlo (VMC and DMC) with correlated Jastrow–Slater-determinant (JSD) and Jastrow–antisymmetrized-geminal-power (JAGP) trial wavefunctions [32] which are discussed in detail in the Supplemental Material [33]. We compare total energies computed using VMC [31,34,35] and DMC [34,36–39], two well-established stochastic methods for many-body electronic structure calculations. In the VMC approach, the total energy is calculated as the expectation value of the Hamiltonian with respect to a chosen trial WF, which is optimized to minimize the variational energy. DMC improves upon this by using a stochastic projection method to evolve the trial WF in imaginary time, effectively filtering out excited-state components and projecting onto the ground-state wave function, within the fixed-node approximation [40,41]. In rectangular simulation cells that break C_3 symmetry and used in this study, the discrete $\mathbf{k}$ mesh can be incommensurate with the Dirac points K and K' , producing a commensurability-induced gap $E_g \propto 1/L_x$ in single-particle spectra. When $L_x = 3n\sqrt{3}d$ with carbon–carbon bond length d , the mesh includes K and $E_g \rightarrow 0$, otherwise a finite E_g appears. We define the RVB pairing energy as the total-energy difference $\delta_P = E_{\text{JAGP}} - E_{\text{JSD}}$ [31,42,43] evaluated in identical cells. VMC systematically favors JAGP for both commensurate (gapless) and incommensurate (finite- E_g) cells. In contrast, DMC shows no RVB energy gain when K is included ($E_g = 0$), while finite E_g stabilizes JAGP at fixed twist. Along an incommensurate, fixed-twist sequence cells that exclude K , an extrapolation of δ_P versus inverse of system size yields $\delta_P \approx -0.4(1)$ mHa per atom. A negative value of δ_P indicates that the JAGP WF captures the effective attraction between opposite spin electrons. The JAGP advantage correlates with E_g and diminishes as $E_g \rightarrow 0$, indicating a geometry-controlled enhancement of RVB correlations in confined twist-selected samples rather than an intrinsic bulk instability of pristine graphene. We

discuss the difference between the calculated pairing energy and superconductivity pairing mechanism. More details on the WFs used and the technical implementation are provided in the previous works [31,42–50].

We construct a rectangular primitive cell consisting of four carbon atoms, defined by the lattice vectors $\mathbf{a} = \sqrt{3}d \hat{\mathbf{x}}$ and $\mathbf{b} = 3d \hat{\mathbf{y}}$, where $d = 1.42 \text{ \AA}$ denotes the nearest-neighbor (NN) C distance [33]. This rectangular cell is twice the size of the conventional hexagonal graphene primitive cell, which contains two atoms and has lattice vectors $\mathbf{a} = d \hat{\mathbf{x}}$ and $\mathbf{b} = -\frac{d}{2} \hat{\mathbf{x}} + \frac{\sqrt{3}d}{2} \hat{\mathbf{y}}$. Importantly, the $\mathbf{a}$ directions of both cells are aligned, which allows a straightforward comparison. Direct comparison between 4-atom rectangular and 2-atom hexagonal unit cells and their Brillouin zones (BZ) are presented in the Supplemental Material [33]. The simulation supercells are constructed by tiling the rectangular primitive cell into $n \times m$ arrays, where n and m are integers satisfying $2 \leq n, m \leq 6$, resulting in simulation cells with atom counts ranging from 16 to 80. These rectangular supercells do not preserve the sixfold rotational ($\pi/3$) symmetry of the infinite graphene lattice. We restrict ourselves to real-valued wave functions obtained at the Γ point, which are appropriate for time-reversal symmetric systems without intrinsic chiral or magnetic order [51].

We found that WF optimization plays a critical role in accurately capturing the pairing energy. We began by systematically optimizing the JSD WF, first optimizing the Jastrow coefficients and two-body correlation terms, followed by the optimization of the Jastrow Gaussian exponents. At this stage, we obtained the standard form of the WF commonly used in QMC simulations, where the Jastrow factor is fully optimized and the Slater determinant is taken from a mean-field approach, DFT in our case. We then proceeded with a full energy optimization of both the Jastrow and Slater determinant components using the linear method [52], followed by an improvement with the SR technique [53]. The resulting energy of the JSD wave function is shown in Fig. 1. The optimized exponents of Jastrow and determinant parts of the JSD WF were then used to build and convert the JAGP WF where the number of MOs is increased to represent a product of independent HF WFs of the C atom [43,44]. The additional MOs were reinitialized by performing an additional DFT simulation. We then reoptimized all the variational parameters by taking the above steps to determine the JAGP WF. We carried out all these steps for the simulation cells used in this work and compared the JAGP energy with JSD. Out of thousands of optimization iterations, we show the last few hundred steps in which the JAGP and JSD energies are competitive [33]. Figure 1 illustrates the VMC energy as a function of the number of optimization steps obtained using JSD and JAGP WFs for two system sizes of $N_{\text{at}} = 80$ and $N_{\text{at}} = 72$ atoms in the simulation cell. The single-particle DFT band structure calculations [33] yield a finite gap with value of $E_g = 2.05 \text{ eV}$ for $N_{\text{at}} = 80$ and zero gap for $N_{\text{at}} = 72$ systems. Both plots demonstrate the energy gain by optimizing the AGP pairing determinant. As it is discussed in the following, although the VMC-JAGP is lower than VMC-JSD, the DMC energies predict a different trend.

The VMC and DMC energies in the thermodynamic limit were obtained by linearly extrapolating the QMC energies as a function of $1/N$, where N is the number of atoms in the

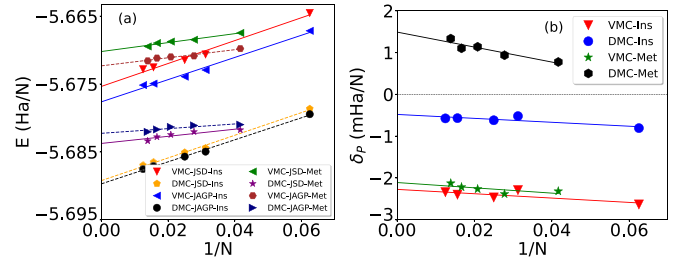


FIG. 2. (a) VMC and DMC energies for finite gap (Ins) and zero gap (Met) systems obtained with JSD and JAGP WFs as a function of system size. (b) VMC and DMC pairing energies for finite gap (Ins) and zero gap (Met) systems obtained with JSD and JAGP WFs as a function of system size. The error bars are smaller than data points size.

simulation cell (Fig. 2). Calculations were performed using both JSD and JAGP WFs for systems with finite and vanishing energy gaps. Our results show that, in the thermodynamic limit, the VMC and DMC energies of the finite-gap $E_g \neq 0$ system are lower than those of the zero-gap $E_g = 0$ system for both types of WFs, indicating enhanced stability of the gapped phase. Figure 2(b) shows the pairing energy δ_P for $E_g \neq 0$ and $E_g = 0$ systems as a function of system size. The VMC- $|\delta_P|$ at the thermodynamic limit is larger than DMC for both systems with $E_g \neq 0$ and $E_g = 0$. The DMC- δ_P at the thermodynamic limit, which is more accurate than VMC, clearly shows no stability of RVB pairing for the $E_g = 0$ system. Our DMC results do not show any energetic stabilization of the JAGP WF relative to JSD for the simulation cell size with the lattice parameter along the x axis $a^* = 3na_0$ with $n = 1, 2$ and a_0 the primitive lattice parameter. For structures characterized by the lattice parameter a^* , the magnitude of the pairing measure $|\delta_P|$ obtained from both VMC and DMC is smaller than for the other geometries examined. Moreover, DMC yields $\delta_P > 0$ for the a^* geometries, indicating the absence of RVB-driven pairing. To assess the influence of the fitting form on δ_P , we fit the size dependence as $\delta_P(N) = \delta_P(\infty) + cN^\alpha$, with c and α as fit parameters, where $\delta_P(N)$ is the pairing energy for system size N . We find that the DMC conclusion that $\delta_P < 0$ for finite-gap systems and $\delta_P > 0$ for $E_g = 0$ is insensitive to the choice of α [33].

In the $a^* = 3na_0$ geometries, the folded $\mathbf{k}$ vectors contain the $\mathbf{k} = (\frac{1}{3}, 0, 0)$ point in primitive reciprocal-lattice units, at which valence and conduction bands touch on the Fermi level. The DFT occupations spectra [54–56] reveal that only at this $\mathbf{k}$ point the degenerate bands just below and above E_F carry ~ 0.5 occupancy, signaling a semimetallic configuration. In contrast, for the other studied geometries, the energy band occupations at every $\mathbf{k}$ point are integer, 1 below E_F and 0 above, resulting in a finite gap phase. To investigate this further, we computed DFT band structures for a series of $\mathbf{k}$ -point meshes, grouping them by whether the number of divisions along k_x was a multiple of three $N_x = 3n$ or not $N_x \neq 3n$, with integer n (Fig. 3). We find that meshes with $N_x \neq 3n$ exhibit a finite gap near the Fermi level, whereas $N_x = 3n$ yields a vanishing gap at the Dirac point. This observation is independent of k_y , as it can be observed from band structures in Fig. 3.

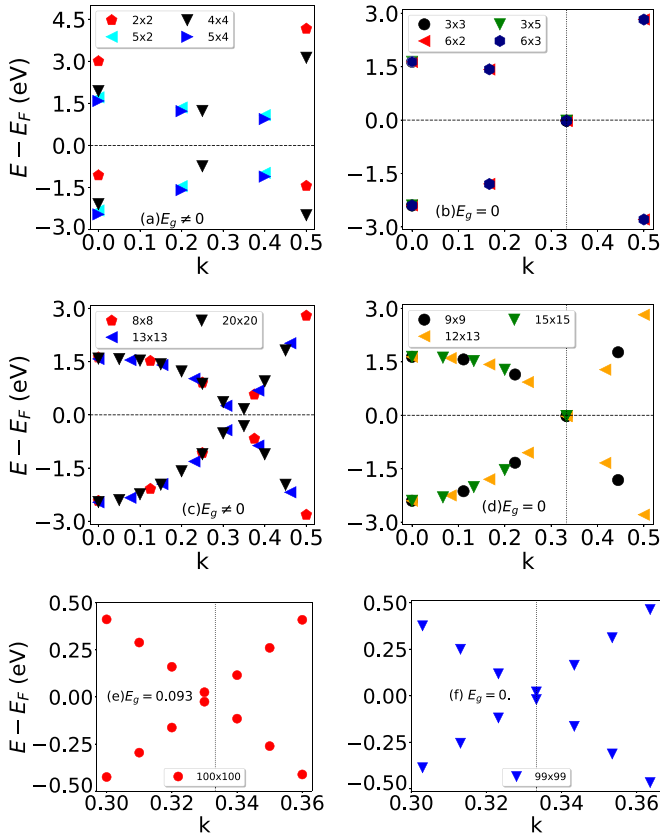


FIG. 3. Single particle energy band as a function of momentum computed by DFT. The valence and conduction band along $\Gamma(0,0) \rightarrow X(\frac{1}{2},0)$ obtained for different $\mathbf{k}$ meshes. The horizontal and vertical lines at $E = 0$ and $k = \frac{1}{3}$ represent the Fermi energy and Dirac point, respectively. (a) and (b) show bands for nonzero $E_g \neq 0$ and zero gap $E_g = 0$ systems for which the RVB pairing energy is obtained by VMC and DMC. (c) and (d) show bands for larger system sizes with nonzero and zero gaps. Comparing the bands obtained by $\mathbf{k}$ mesh 13×13 and 12×13 demonstrate that vanishing gap only depends on k_x . (e) and (f) show bands near the Dirac point obtained using $\mathbf{k}$ meshes of 100×100 with $E_g = 0.093$ eV and 99×99 with $E_g = 0$.

The ground state DMC energy depends on the nodal surface of the trial WF. The nodal surface of the WFs used in our DMC simulations is determined by the occupied subspace of single-particle orbitals and any unitary rotation within that subspace leaves the node unchanged. Including the Jastrow correlation function in the WF does not also affect the nodal surface. Appearance of a gap near the Fermi energy in one-particle spectra separates the occupied subspace from the unoccupied. The degenerate occupied Dirac-cone states on the Fermi energy changes the nodal surface of the WF and consequently introduces a difference between DMC-JSD and DMC-JAGP energies. The key point is that a vanishing gap and strictly linear single-particle dispersion $E(k)$ occur only when the $\mathbf{k}$ mesh samples the Dirac point exactly meaning that the Brillouin zone coordinates containing recurring decimal $1/3$ fractions. For meshes with $N_x \neq 3n$ in reciprocal space, or equivalently, real-space periodicities with $a^* \neq 3na_0$, the Dirac point is not sampled, the ideal linear $E(k)$ is perturbed,

and a gap opens near the Fermi level. For incommensurate grids with $N_x \notin 3\mathbb{Z}$ where K is not sampled, the geometry-induced gap E_g decreases as the system size grows, as $E_g \propto 1/L_x \propto 1/N_x$, and is therefore arbitrarily small but positive at any finite size. It becomes zero only in the commensurate case $N_x = 3n$ equivalently, when the real-space period satisfies the corresponding commensurability condition or in the limit $L_x \rightarrow \infty$. This can be observed from Figs. 3(e) and 3(f) showing the bands near the Dirac point for $\mathbf{k}$ meshes of 100×100 , with ~ 0.1 eV gap, and 99×99 with zero gap, respectively. Note that the gap value here is taken from DFT, which is well known to misestimate band gaps [33]. The precise magnitude, and even the character, of the gap should be determined with many-body approaches.

Our results indicate that selecting certain longitudinal dimensions for a rectangular graphene sheet opens a finite, size-dependent energy gap and, in turn, yields an attractive RVB-like pairing energy. In this regime, the finite cell's BZ does not sample the Dirac point exactly. Instead it captures nearby k points where the gap appears. To illustrate, we performed DFT simulations for two system sizes of 676 with lattice parameters $a = 3.197$ and $b = 5.538$ nm, and 624 with lattice parameters $a = 2.951$ and $b = 5.538$ nm, and C atoms corresponding to $\mathbf{k}$ meshes of 13×13 and 12×13 , respectively, with band structures shown in Figs. 3(c) and 3(d). DFT further indicates that the 676-atom system size is insulating with a gap of $E_g = 0.69$ eV, whereas the 624-atom system size remains gapless with a degeneracy at the Fermi level [33]. Guided by our QMC results, we therefore expect RVB pairing to be stabilized in the 676-atom system, consistent with the emergence of a strongly correlated state. A small gap appearing in a graphene sample reduces low-energy density of states (DOS), therefore disfavoring weak-coupling pairing and consequently changing the balance between s or d wave states and screening. Our results indicate that a strongly correlated state in a geometrical driven finite gap graphene sheet can be stabilized through RVB mechanisms. Breaking the linear behavior of $E(k)$ and opening a gap near the Fermi energy can introduce other properties which require further studies. For instance, a small gap replaces massless, chiral Dirac fermions by massive ones, turning on Berry curvature and valley physics, and possibly suppressing Klein tunneling [5,6] which are depend on the nature of the gap.

The extrapolated DMC δ_P values are taken in the fixed-twist thermodynamic limit $N \rightarrow \infty$ while keeping the geometry induced gap E_g fixed either $E_g > 0$ when the k mesh misses K or $E_g = 0$ when it includes K . This corresponds to large, twist-selected samples whose low-energy spectrum is set by geometry, not to the twist-averaged bulk. Although twist-averaged energies were not calculated, based on Dirac scaling we predict that the twist-averaged pairing energy would destabilize in the bulk limit. Graphene is very unique in this sense that conduction and valence bands only touch at the Dirac points. There is no Fermi crossing. Performing twist averaging for DMC energies using 10–20 twists yields an energy very close to that of a gapped system because most twists belong to a nonzero gap system. This can also be observed from the relatively good linear behavior of the energy of metallic systems versus $1/N$ [Fig. 2(a)], since they are not really metallic, according to the band-theory definition, but

semimetallic. True semimetallic behavior can be restored only with a very large number of twists, which is very challenging for DMC calculations at large N .

Similar commensurability physics can appear in different devices. For instance, in armchair nanoribbons and strips, the subband structure depends on width modulo three, yielding $E_g = 0$ or $E_g > 0$ with $E_g \propto 1/W$ [57,58]. Also, in rectangular cavities and gate-defined constrictions, the standing-wave quantization along the short direction produces $E_g \sim \hbar v_F/L$ for typical aspect ratios [59,60]. Moreover in patterned-gate or weak superlattice devices, a rectangular mini-Brillouin zone can exclude K or K' generating $E_g > 0$ that scales down with device size [61,62].

A finite limiting value of $\text{DMC-}\delta_P$ in the fixed-twist sense means that short-range singlet correlations encoded by the JAGP nodal structure remain energetically advantageous for that geometry. Importantly, this quantity is not necessarily a superconducting condensation energy and not evidence of a spin-liquid phase. It is a measure of how much a more flexible local-pairing ansatz lowers the ground-state energy under a particular spectral quantization. Superconductivity requires off-diagonal long-range order in the two-body density matrix, a finite phase stiffness and superfluid weight, and broken global $U(1)$ symmetry, which were not included in our DMC simulations. The JAGP can variationally

lower the energy by capturing short-range singlet correlations, even in a normal state, without implying long-range order. Consistent with this, the JAGP advantage tracks the shell gap and vanishes as $E_g \rightarrow 0$, meaning it is amplified by geometric quantization that suppresses low-energy Dirac excitations but does not signal a bulk broken-symmetry phase.

In summary, our results show that geometry can tilt the energetic balance toward local singlet pairing. This identifies a design knob for nanoscale graphene, shapes, aspect ratios, or mild superlattice modulations that produce a small single-particle gap can amplify short-range pairing tendencies and lower the many-body energy with RVB-like correlations. This is relevant for engineered devices, proximitized heterostructures, or platforms exploring correlation-enhanced phenomena.

We acknowledge the support of the Leverhulme Trust under Grant Agreement RPG-2023-253. S.A. and T.D.K. acknowledge the computing time provided to them on the high-performance computers Noctua2 at the NHR Center in Paderborn (PC2).

Data availability. The data that support the findings of this article are openly available [63], embargo periods may apply.

-
- [1] K. Novoselov, A. Geim, S. Morozov, D. Jiang, Y. Zhang, S. Dubonos, I. Grigorieva, and A. Firsov, Electric field effect in atomically thin carbon films, *Science* **306**, 666 (2004).
 - [2] A. Geim and K. Novoselov, The rise of graphene, *Nat. Mater.* **6**, 183 (2007).
 - [3] A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, The electronic properties of graphene, *Rev. Mod. Phys.* **81**, 109 (2009).
 - [4] K. Novoselov, A. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. Grigorieva, S. Dubonos, and A. Firsov, Two-dimensional gas of massless Dirac fermions in graphene, *Nature (London)* **438**, 197 (2005).
 - [5] V. N. Kotov, B. Uchoa, V. M. Pereira, F. Guinea, and A. H. C. Neto, Electron-electron interactions in graphene: Current status and perspectives, *Rev. Mod. Phys.* **84**, 1067 (2012).
 - [6] S. D. Sarma, S. Adam, E. H. Hwang, and E. Rossi, Electronic transport in two-dimensional graphene, *Rev. Mod. Phys.* **83**, 407 (2011).
 - [7] Y. Cao, V. Fatemi, S. Fang, K. Watanabe, T. Taniguchi, E. Kaxiras, and P. Jarillo-Herrero, Unconventional superconductivity in magic-angle graphene superlattices, *Nature (London)* **556**, 43 (2018).
 - [8] S. Azadi, N. D. Drummond, and S. M. Vinko, Quantum Monte Carlo study of the phase diagram of the two-dimensional uniform electron liquid, *Phys. Rev. B* **110**, 245145 (2024).
 - [9] S. Azadi, N. D. Drummond, A. Principi, R. V. Belosludov, and M. S. Bahramy, Quantum Monte Carlo study of the quasiparticle effective mass of the two-dimensional uniform electron liquid, *Phys. Rev. B* **112**, 075141 (2025).
 - [10] K. Novoselov, V. Falko, L. Colombo, P. Gellert, M. Schwab, and K. Kim, A roadmap for graphene, *Nature (London)* **490**, 192 (2012).
 - [11] F. Guinea, M. Katsnelson, and A. Geim, Energy gaps and a zero-field quantum Hall effect in graphene by strain engineering, *Nat. Phys.* **6**, 30 (2010).
 - [12] K. Novoselov, Z. Jiang, Y. Zhang, S. Morozov, H. Stormer, U. Zeitler, J. Maan, G. Boebinger, P. Kim, and A. Geim, Room-temperature quantum Hall effect in graphene, *Science* **315**, 1379 (2007).
 - [13] J. E. Drut and T. A. Lähde, Is graphene in vacuum an insulator? *Phys. Rev. Lett.* **102**, 026802 (2009).
 - [14] E. Rotenberg, A. Bostwick, T. Ohta, J. L. McChesney, T. Seyller, and K. Horn, Origin of the energy bandgap in epitaxial graphene, *Nat. Mater.* **7**, 258 (2008).
 - [15] S. Sorella and E. Tosatti, Semi-metal-insulator transition of the Hubbard model in the honeycomb lattice, *Europhys. Lett.* **19**, 699 (1992).
 - [16] S. Sachdev, in *Low Dimensional Quantum Field Theories for Condensed Matter Physicists*, edited by L. Yu, S. Lundqvist, and G. Morandi (World Scientific, Singapore, 1995).
 - [17] Z. Meng, T. Lang, S. Wessel, F. Assaad, and A. Muramatsu, Quantum spin liquid emerging in two-dimensional correlated Dirac fermions, *Nature (London)* **464**, 847 (2010).
 - [18] M.-T. Tran and K.-S. Kim, Spin liquids in graphene, *Phys. Rev. B* **83**, 125416 (2011).
 - [19] P. A. Lee, N. Nagaosa, and X.-G. Wen, Doping a Mott insulator: Physics of high-temperature superconductivity, *Rev. Mod. Phys.* **78**, 17 (2006).

- [20] S. Pathak, V. B. Shenoy, and G. Baskaran, Possible high-temperature superconducting state with a $d+id$ pairing symmetry in doped graphene, *Phys. Rev. B* **81**, 085431 (2010).
- [21] S. Lisi, X. Lu, T. Benschop, T. A. de Jong, P. Stepanov, J. R. Duran, *et al.*, Observation of flat bands in twisted bilayer graphene, *Nat. Phys.* **17**, 189 (2021).
- [22] P. W. Anderson, The resonating valence bond state in La_2CuO_4 and superconductivity, *Science* **235**, 1196 (1987).
- [23] G. Baskaran and P. W. Anderson, Gauge theory of high-temperature superconductors and strongly correlated Fermi systems, *Phys. Rev. B* **37**, 580 (1988).
- [24] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, NY, 1960).
- [25] C. Glittum, A. Štrkalj, D. Prabhakaran, P. Goddard, C. D. Batista, and C. Castelnovo, A resonant valence bond spin liquid in the dilute limit of doped frustrated mott insulators, *Nat. Phys.* **21**, 1211 (2025).
- [26] P. W. Anderson, G. Baskaran, Z. Zou, and T. Hsu, Resonating-valence-bond theory of phase transitions and superconductivity in La_2CuO_4 -based compounds, *Phys. Rev. Lett.* **58**, 2790 (1987).
- [27] Y. Zhou, K. Kanoda, and T.-K. Ng, Quantum spin liquid states, *Rev. Mod. Phys.* **89**, 025003 (2017).
- [28] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Spin liquid state in an organic Mott insulator with a triangular lattice, *Phys. Rev. Lett.* **91**, 107001 (2003).
- [29] M. R. Norman, *Colloquium: Herbertsmithite and the search for the quantum spin liquid*, *Rev. Mod. Phys.* **88**, 041002 (2016).
- [30] M. Casula and S. Sorella, Improper s -wave symmetry of the electronic pairing in iron-based superconductors by first-principles calculations, *Phys. Rev. B* **88**, 155125 (2013).
- [31] F. Becca and S. Sorella, *Quantum Monte Carlo Approaches for Correlated Systems* (Cambridge University, Cambridge, UK, 2017).
- [32] J. P. Perdew and A. Zunger, Self-interaction correction to density-functional approximations for many-electron systems, *Phys. Rev. B* **23**, 5048 (1981).
- [33] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/hmmc-nhdl> for more details of our calculations and additional figures and data.
- [34] W. M. C. Foulkes, L. Mitás, R. J. Needs, and G. Rajagopal, Quantum Monte Carlo simulations of solids, *Rev. Mod. Phys.* **73**, 33 (2001).
- [35] S. Fahy, X. W. Wang, and S. G. Louie, Variational quantum Monte Carlo nonlocal pseudopotential approach to solids: Formulation and application to diamond, graphite, and silicon, *Phys. Rev. B* **42**, 3503 (1990).
- [36] D. M. Ceperley, Ground state of the fermion one-component plasma: A Monte Carlo study in two and three dimensions, *Phys. Rev. B* **18**, 3126 (1978).
- [37] D. M. Ceperley and B. J. Alder, Ground state of the electron gas by a stochastic method, *Phys. Rev. Lett.* **45**, 566 (1980).
- [38] A. Annaberdiyev, G. Wang, C. A. Melton, M. C. Bennett, L. Shulenburger, and L. Mitás, A new generation of effective core potentials from correlated calculations: 3d transition metal series, *J. Chem. Phys.* **149**, 134108 (2018).
- [39] M. C. Bennett, C. A. Melton, A. Annaberdiyev, G. Wang, L. Shulenburger, and L. Mitás, A new generation of effective core potentials for correlated calculations, *J. Chem. Phys.* **147**, 224106 (2017).
- [40] C. A. Melton and L. Mitás, Quantum Monte Carlo with variable spins: Fixed-phase and fixed-node approximations, *Phys. Rev. E* **96**, 043305 (2017).
- [41] M. Casula, Beyond the locality approximation in the standard diffusion Monte Carlo method, *Phys. Rev. B* **74**, 161102(R) (2006).
- [42] K. Nakano, C. Attaccalite, M. Barborini, L. Capriotti, M. Casula, E. Coccia, M. Dagrada, C. Genovese, Y. Luo, G. Mazzola, A. Zen, and S. Sorella, Turborvb: A many-body toolkit for *ab initio* electronic simulations by quantum Monte Carlo, *J. Chem. Phys.* **152**, 204121 (2020).
- [43] M. Marchi, S. Azadi, M. Casula, and S. Sorella, Resonating valence bond wave function with molecular orbitals: Application to first-row molecules, *J. Chem. Phys.* **131**, 154116 (2009).
- [44] M. Marchi, S. Azadi, and S. Sorella, Fate of the resonating valence bond in graphene, *Phys. Rev. Lett.* **107**, 086807 (2011).
- [45] M. Casula and S. Sorella, Geminal wave functions with jastrow correlation: A first application to atoms, *J. Chem. Phys.* **119**, 6500 (2003).
- [46] S. Azadi, M. S. Bahramy, and T. D. Kühne, Electron correlation effects and spin-liquid state in the herbertsmithite kagome lattice, *Phys. Rev. Res.* **7**, 013165 (2025).
- [47] S. Azadi, C. Cavazzoni, and S. Sorella, Systematically convergent method for accurate total energy calculations with localized atomic orbitals, *Phys. Rev. B* **82**, 125112 (2010).
- [48] S. Sorella, N. Devaux, M. Dagrada, G. Mazzola, and M. Casula, Geminal embedding scheme for optimal atomic basis set construction in correlated calculations, *J. Chem. Phys.* **143**, 244112 (2015).
- [49] S. Azadi, R. Singh, and T. D. Kühne, Resonating valence bond quantum Monte Carlo: Application to the ozone molecule, *Int. J. Quantum Chem.* **115**, 1673 (2015).
- [50] M. Casula, C. Attaccalite, and S. Sorella, Correlated geminal wave function for molecules: An efficient resonating valence bond approach, *J. Chem. Phys.* **121**, 7110 (2004).
- [51] L. Mitás, Quantum Monte Carlo pair orbital wave functions for periodic systems, *Phys. Rev. Lett.* **135**, 126401 (2025).
- [52] C. J. Umrigar, J. Toulouse, C. Filippi, S. Sorella, and R. G. Hennig, Alleviation of the fermion-sign problem by optimization of many-body wave functions, *Phys. Rev. Lett.* **98**, 110201 (2007).
- [53] S. Sorella, Green function Monte Carlo with stochastic reconfiguration, *Phys. Rev. Lett.* **80**, 4558 (1998).
- [54] P. Giannozzi, *et al.*, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- [55] P. Giannozzi, *et al.*, Advanced capabilities for materials modeling with QUANTUM ESPRESSO, *J. Phys.: Condens. Matter* **29**, 465901 (2017).
- [56] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [57] Y.-W. Son, M. L. Cohen, and S. G. Louie, Energy gaps in graphene nanoribbons, *Phys. Rev. Lett.* **97**, 216803 (2006).
- [58] M. Y. Han, B. Ozyilmaz, Y. Zhang, and P. Kim, Energy band-gap engineering of graphene nanoribbons, *Phys. Rev. Lett.* **98**, 206805 (2007).

- [59] L. A. Ponomarenko, F. Schedin, M. I. Katsnelson, R. Yang, E. W. Hill, K. S. Novoselov, and A. K. Geim, Chaotic Dirac billiard in graphene quantum dots, *Science* **320**, 356 (2008).
- [60] N. Tombros, A. Veligura, J. Junesch, M. H. D. Guimaraes, I. J. Vera-Marun, H. T. Jonkman, and B. J. van Wees, Quantized conductance of a suspended graphene nanoconstriction, *Nat. Phys.* **7**, 697 (2011).
- [61] L. A. Ponomarenko, R. V. Gorbachev, G. L. Yu, D. C. Elias, R. Jalil, A. A. Patel, A. Mishchenko, A. S. Mayorov, C. R. Woods, J. R. Wallbank, M. Mucha-Kruczynski, B. A. Piot, M. Potemski, I. V. Grigorieva, K. S. Novoselov, F. Guinea, V. I. Fal'ko, and A. K. Geim, Cloning of Dirac fermions in graphene superlattices, *Nature (London)* **497**, 594 (2013).
- [62] M. Yankowitz, J. Xue, D. Cormode, J. D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, P. Jarillo-Herrero, P. Jacquod, and B. J. LeRoy, Emergence of superlattice Dirac points in graphene on hexagonal boron nitride, *Nat. Phys.* **8**, 382 (2012).
- [63] S. Azadi, Github, <https://github.com/arshamsam>.