

Estimates of effective Hubbard model parameters for C₂₀ isomersFei Lin¹ and Erik S. Sørensen²¹Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA²Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada L8S 4M1

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We report on an effective Hubbard Hamiltonian approach for the study of electronic correlations in C₂₀ isomers—cage, bowl, and ring—with quantum Monte Carlo and exact diagonalization methods. The tight-binding hopping parameter, t , in the effective Hamiltonian is determined by a fit to density-functional theory calculations, and the on-site Coulomb interaction, U/t , is determined by calculating the isomers' affinity energies, which are compared to experimental values. For the C₂₀ fullerene cage we estimate $t_{\text{cage}} \approx 0.68\text{--}1.36$ eV and $(U/t)_{\text{cage}} \approx 7.1\text{--}12.2$. The resulting effective Hamiltonian is then used to study the shift of spectral peaks in the density of states of neutral and one-electron-doped C₂₀ isomers. Energy gaps are also extracted for possible future comparison with experiments.

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I. INTRODUCTION

The successful synthesis of gas phase C₂₀ molecules displaying the dodecahedral fullerene cage structure¹ has induced considerable research interest in this smallest fullerene molecule partly because of the superconducting property of electron-doped C₆₀ materials² in the same fullerene family and partly because previous theoretical speculations^{3–5} about the existence of such a cage molecule were confirmed. In the experiment,¹ three major C₂₀ isomers—cage, bowl, and ring structures—were produced. See Fig. 1 for the molecular structures. Photoelectron spectra (PES) were also measured for all three brominated and one-electron-doped isomers (C₂₀⁻). Affinity energies (AE, see definition below) were then extracted from the PES figure, giving $AE_{\text{cage}}=2.25$ eV, $AE_{\text{bowl}}=2.17$ eV, and $AE_{\text{ring}}=2.44$ eV, respectively. Since PES spectra reflect both the isomers' geometric character and the strength of electronic correlation inside the molecules, it is a unique opportunity to investigate the interplay between geometry and electronic correlations in the three isomers. Here, we shall do this by estimating the parameters in an effective Hubbard model description of these isomers parametrized in terms of the on-site repulsion, U , and hopping integral, t . We find that for the geometry with the highest curvature, the fullerene cage, correlations effects as measured by U/t are relatively important. Experiments have also shown evidence for solid phases of C₂₀ fullerene cage,^{6,7} further emphasizing the need for understanding strong correlation effects in this isomer.

The possibility of superconductivity arising from a purely electronic mechanism in the C₆₀ fullerenes was suggested in the early 1990s (Ref. 8) and supported by perturbative calculations^{8,9} starting from a one-band Hubbard model. In this picture superconductivity arises from strong correlation effects since the many-body energy levels favor electrons residing on the same molecule as opposed to different molecules, resulting in a negative pair-binding energy. However, extensive numerical work¹⁰ has shown that the pair-binding energy in C₆₀ materials is likely *positive* for $U/t \leq 4.5$ with larger values of U/t , inaccessible due to an increasingly severe sign problem. Comparatively, C₂₀ has a larger curvature,

and correlation effects measured in terms of U/t are therefore likely much more important since the curvature will decrease t and thereby increase U/t . We previously studied electron correlation effects in the C₂₀ fullerene cage¹¹ start-

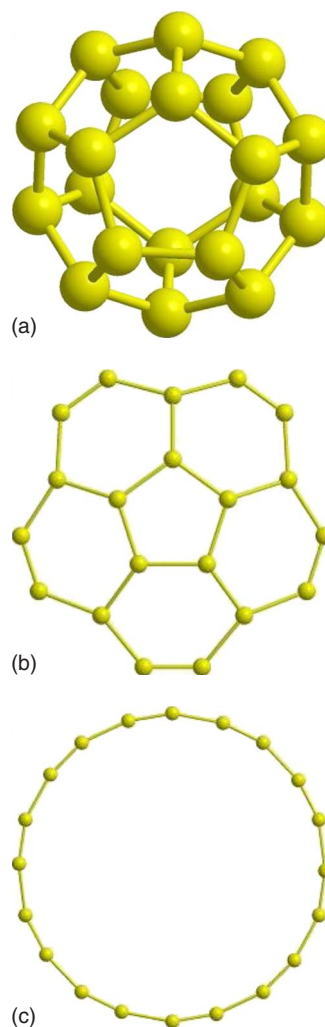


FIG. 1. (Color online) Molecular structures of C₂₀ isomers: (a) cage, (b) bowl, and (c) ring.

ing from a one-band Hubbard model defined in Eq. (1). For the whole range of $0 < U/t < \infty$, we find that the pair-binding energy is always *positive*, ruling out the possibility of superconductivity induced solely by an electronic mechanism. With increasing U/t there is, however, a very interesting metal-insulator transition predicted¹¹ to occur around $U/t \sim 4.1$ in molecular solids formed with the C_{20} fullerene. Experiments have shown evidence for such solid phases of C_{20} .^{6,7} We expect that most of the strong correlation effects are fully captured by a one-band Hubbard model with a single *uniform* hopping integral. In order to develop predictive models of C_{20} materials and to determine whether such materials will display metallic or insulating behavior, it is then crucial to estimate how large U/t is for the C_{20} molecule, which is the main purpose of this paper.

Mean-field density-functional theory (DFT) calculations have yielded conflicting predictions of the relative stability of C_{20} isomers. This suggests that electron correlations, which are only approximately treated in the DFT calculations, could be very important in the prediction of the electronic structure of C_{20} isomers even though the geometry of the different isomers is fully captured in the DFT calculations. We are, therefore, inspired to study the isomers with an effective Hamiltonian approach, where a Huckel Hamiltonian is complemented with an on-site electron correlation term, i.e., the one-band Hubbard model defined on a single C_{20} molecule as

$$H = - \sum_{\langle ij \rangle \sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \varepsilon_p \sum_i n_i, \quad (1)$$

where $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) is an electron creation (annihilation) operator with spin σ on site i , indices i, j runs over 20 sites of the isomers, t_{ij} is the hopping integral between nearest-neighbor (NN) carbon atoms i and j , U is the on-site electron correlation, $n_i = n_{i\uparrow} + n_{i\downarrow}$ is the number of electrons on site i , and ε_p is the on-site electronic energy due to the core ion and electrons in the carbon atom. According to Ref. 12, we set $\varepsilon_p = -8.97$ eV. This on-site electronic energy term is a constant as long as the total electron number in the molecules is fixed and is not important in calculating, e.g., the pair-binding energy,¹¹ but needs to be taken into account when calculating the affinity energy of the molecules defined as

$$\text{AE} = E(20) - E(21), \quad (2)$$

where $E(N)$ is the internal energy of the molecule filled with N electrons from $2p$ atomic orbitals.

The idea of fitting a tight-binding Huckel Hamiltonian to DFT energy levels for a fullerene molecule is not new and has been employed in, e.g., Refs. 13 and 14. However, inclusion of an on-site Coulomb interaction in the tight-binding model for the fullerene molecule has not been very well studied due to the difficulty of performing reliable calculations in the presence of such a term. In particular, the question of what value the on-site interaction U should take has not been answered for C_{20} isomers. In light of the metal-insulator transition predicted¹¹ to occur around $U/t=4.1$, a correct determination of U/t is crucial for modeling C_{20} -based materials. Addressing this question is our main goal here. The paper is organized as follows. First, since we

want the tight-binding t term (Huckel Hamiltonian) to reflect the geometric character of each of the isomers, which is contained in the DFT energy levels, we fit the Huckel energy levels to energy levels obtained from DFT. This allows us to determine the effective value of t for the three isomers. Here we assume *uniform* hopping integrals t inside the cage and bowl molecules for the Huckel Hamiltonian, although within the DFT approach for the bowl isomer the hopping integrals are *not* uniform⁵ even in the absence of any Jahn-Teller distortion. We expect this simplification for the Huckel approach to be of only minor importance for the bowl and the cage. However, for the ring isomer, DFT calculations show that the ring structure is dimerized⁵ with alternating long and short bonds between NN carbon atoms, which leads to a filled highest occupied molecular orbital (HOMO), i.e., an insulating molecule, in contrast to the uniform bonding case, where the HOMO is not completely filled (the molecule is metallic). We, therefore, consider two different hopping integrals for the ring Huckel Hamiltonian. As mentioned, inhomogeneous hopping integrals are always considered in the DFT calculations. We then study the effect of electron correlation in the neutral isomers by calculating the single-particle excitation spectra with different correlation strengths ($U/t = 2, 3, 4, 5$) and show the difference between quantum Monte Carlo (QMC) and DFT spectra for the neutral isomers. To complete our effective Hamiltonian approach, we proceed to estimate the on-site Coulomb interaction strength U by calculating the electron affinity energies of the isomers and comparing them to the experimental values. This allows us to determine U/t for each isomer, and we can then study the effect of one-electron doping on the single-particle excitation spectra with QMC simulations. We compare the resulting QMC spectra to results obtained from DFT. These spectra should be directly comparable to possible future experimental PES and inverse PES spectra.

II. ESTIMATION OF THE HUCKEL HOPPING INTEGRAL, t

Different molecular geometries of C_{20} isomers determine different NN hopping integrals, t 's, in the Huckel description of molecules. In this section, we estimate approximate values of t 's for the cage, bowl, and ring structures of C_{20} molecules by comparing tight-binding Huckel energy diagrams ($U=0$) with the energy levels from DFT calculations. In DFT calculations for the cage and bowl, $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals are considered, and the calculations are performed with the widely used ABINIT code.¹⁵ Since there are four orbitals per carbon atom in the DFT calculation, the resulting energy levels are a mixture of σ and π bonds. The σ bonds have either very low or very high energies. Energy levels around the Fermi energy mainly consist of π bonds, which we use to construct the Huckel Hamiltonian. The comparison of energy levels between DFT and tight-binding Huckel Hamiltonian should, therefore, be made around Fermi energy. Table I shows such a comparison. To fit the Huckel hopping parameters t , we set equal the *smallest* energy gap of the tight-binding Huckel Hamiltonian with an equivalent gap in the DFT results. The degeneracy of the levels are

TABLE I. Comparison of energy levels around the Fermi energy from DFT calculation and Huckel Hamiltonian on the C_{20} isomers. The energy from DFT is in units of eV. D is the degeneracy degree of the corresponding energy level, and N_e is the number of electrons occupying these energy levels. For each isomer, the energy levels are listed in descending order.

	DFT			Huckel ($U=0$)		
	E (eV)	D	N_e	E/t	D	N_e
Cage	1.72766	3	0	2.23607	3	0
	0.37579	1	0	2.0	4	0
	-0.98560	4	2	0.0	4	2
	-6.65895	5	10	-1.0	5	10
Bowl	-2.15325	1	0	1.0	1	0
	-2.50728	1	0	0.47725	2	0
	-5.00612	1	2	-0.73764	2	4
	-5.02272	1	2	-0.77748	2	4
Ring	-6.96644	1	0	0.63303	2	0
	-7.54251	1	0	0.14400	1	0
	-8.45383	1	2	-0.14400	1	2
	-8.94745	1	2	-0.63303	2	4

important here, and since the variation in the hopping integrals in the DFT approach in some cases will split levels, the equivalent gap in the DFT approach is *not necessarily* the smallest gap. In studies of strong correlation effects, it is highly desirable to use the simplest possible model. Since for the fullerene cage the DFT and the tight-binding model with *uniform* hopping at $U=0$ both predict a half-filled HOMO level and metallic behavior, we have not found it necessary to include variations in the hopping integral. The same is true for the bowl where a filled HOMO level is found. However, as previously mentioned, for the ring the two approaches disagree, and we are therefore forced to include a variation in the hopping integrals for the ring, which we describe in detail below.

We begin by discussing the fullerene cage. Here we find a half-filled fourfold degenerate HOMO level, and hence a metal in both the DFT (-0.98560 eV) and tight-binding ($0t_{\text{cage}}$) results. In the tight-binding approach the first-excited level is fourfold degenerate at $2t_{\text{cage}}$. Assuming that this fourfold level is split into a high-lying fourfold and a lower-lying nondegenerate level due to slight variations in the effective hopping integrals in the DFT approach, the equivalent gap in the DFT approach should be from the fourfold level at -0.98560 eV to some average of the threefold and nondegenerate excited levels. In the extreme case we neglect the nondegenerate level and we then see that this gap should be close to the $(1.72766+0.98560)$ eV= 2.71326 eV from which we infer that $t_{\text{cage}} \approx 1.36$ eV. Here we have taken the gap in the DFT calculations to go from the fourfold degenerate level to the threefold degenerate level. Given the splitting of the excited levels in the DFT approach, it seems plausible that this is a maximal value for the gap. However, in the absence of analytical results for the splitting of the levels in the DFT approach we note that this is not an exact

bound. The estimate $t_{\text{cage}} \approx 1.36$ eV is then likely an upper bound on the hopping integral. An extreme *lower* bound on t_{cage} can be obtained if we use the smallest gap of $(0.37579+0.98560)$ eV= 1.36139 eV in the DFT approach, yielding $t_{\text{cage}}^{\text{min}} \approx 0.68$ eV. Given the large splitting of the nondegenerate level from the threefold level, this lower bound seems very unlikely to be attained and a more realistic value for t_{cage} is likely close to the upper bound of 1.36 eV, which we mainly focus on in the following.

We next turn to the bowl where one in both the DFT and tight-binding approach ($U=0$) finds a filled HOMO level and hence an insulator. For the bowl we compare the tight-binding gap of $(0.47725+0.73764)t_{\text{bowl}}=1.21489t_{\text{bowl}}$ from a twofold degenerate level to another twofold degenerate level with the $(-2.15325+5.02272)$ eV= 2.86947 eV gap in the DFT results yielding $t_{\text{bowl}} \approx 2.36$ eV. As for the fullerene cage, we have here assumed that both twofold degenerate levels are slightly split in the DFT approach and we have used the largest reasonable value for the equivalent gap in the DFT approach. Following the discussion of the hopping integral for the fullerene cage, we again expect the estimate $t_{\text{bowl}} \approx 2.36$ eV to be an upper bound. In this case, a reasonable *lower* bound on the hopping integral can be obtained by taking the smallest gap in the DFT approach of $(-2.50728+5.00612)$ eV= 2.49884 eV, resulting in $t_{\text{bowl}}^{\text{min}} \approx 2.06$ eV, a relatively modest variation from our previous maximal estimate.

Finally we turn to a discussion of the ring molecule. As mentioned, in this case a *uniform* tight-binding model would predict a half-filled HOMO level where the DFT approach shows a filled HOMO level. We are therefore forced to include a staggering in the hopping integrals in the tight-binding approach. For the ring DFT calculation, we first generate a pseudopotential¹⁶ for the carbon atom, with four electrons ($1s^2 2s^2$) in the core state and two electrons ($2p^2$) in the valence state. The resulting pseudopotential is then fed to the ABINIT (Ref. 15) to carry out DFT calculations on the two valence orbitals. On the tight-binding calculation side, we use two hopping integrals, t_l and t_s , to represent the hopping integrals of the alternating long ($b_l=2.609$ Bohr) (Ref. 5) and short ($b_s=2.260$ Bohr) (Ref. 5) bonds, respectively. Let the average of the two bonds be $b=(b_l+b_s)/2=2.435$ Bohr. We then parametrize¹¹ the two hopping integrals as $t_x/t_{\text{ring}}=1-(b_x-b)/b$, where $x=l,s$ and t_{ring} is the average hopping integral. With this parametrization we find $t_l=0.928t_{\text{ring}}$ and $t_s=1.072t_{\text{ring}}$. From Table I we see that both DFT and tight-binding calculations now give an insulating molecule. If we again compare the tight-binding gap of $(0.14400+0.14400)t_{\text{ring}}=0.288t_{\text{ring}}$ from a nondegenerate level to another nondegenerate level with the gap between two nondegenerate levels in the DFT results of $(-7.54251+8.45383)$ eV= 0.91132 eV, it results in an average $t_{\text{ring}} \approx 3.16$ eV.

We see that compared to the other isomers the hopping integral is *significantly smaller* in the fullerene cage isomer due to the large curvature of the molecule that reduces the NN overlap of the $2p$ orbitals. Consequently, t_{cage} for the C_{20} fullerene is also significantly smaller than what was found for the much bigger and less curved C_{60} where one observes $t_{C_{60}}=2.50$ eV according to our calculation with ABINIT as

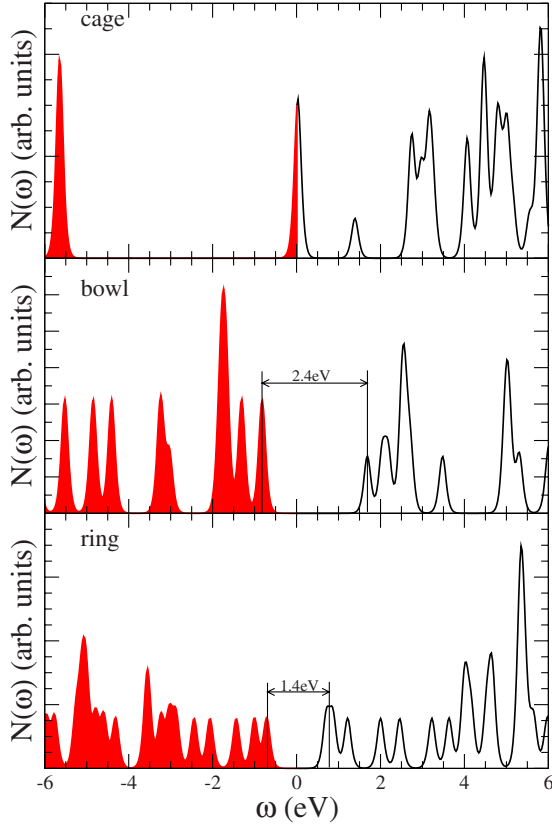


FIG. 2. (Color online) DOS from DFT for neutral cage, bowl, and ring C_{20} isomers. Fermi energy is located at $\omega=0$. Shaded areas are occupied by electrons.

well as Ref. 14 or 2.72 eV according to Satpathy's early calculation.¹³ It is also noteworthy that our estimate is likely an upper bound on t_{cage} . We also note that $t_{\text{ring}} \sim 2t_{\text{cage}}$, which reflects the fact that t_{ring} is the hopping integral of four $2p$ orbitals as apposed to t_{cage} being the hopping integral of two $2p_{\pi}$ orbitals.

III. DENSITY OF STATES FROM DFT CALCULATION

Before we study the effect of electronic correlation with QMC, we calculate the density of states (DOS) for the neutral C_{20} isomers within DFT, shown in Fig. 2. We see that both the bowl and ring are insulators, with energy gaps $\Delta_{\text{bowl}}^{\text{DFT}}=2.4$ eV and $\Delta_{\text{ring}}^{\text{DFT}}=1.4$ eV for the neutral molecule. The fullerene cage isomer is, however, metallic. Electron correlations are typically underestimated in DFT calculations, and it therefore seems reasonable to assume that the inclusion of on-site electronic correlations would enlarge the gap, eventually turning the cage C_{20} isomer into an insulator. Such an effect was shown to occur in Ref. 11.

IV. EFFECT OF ON-SITE CORRELATION

As mentioned, DFT calculations typically underestimate electron correlations. However, with the overlap integral, t , determined we can attempt to more closely describe the physics in the vicinity of the Fermi energy by using an ef-

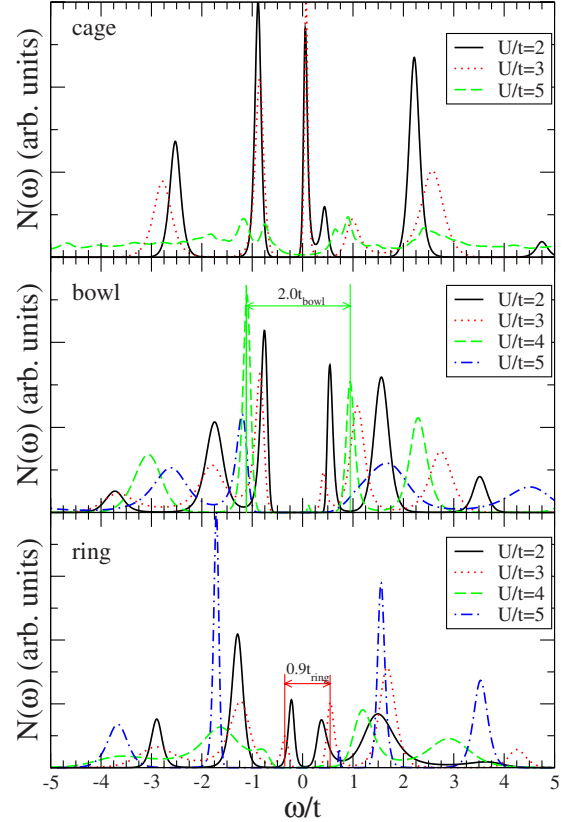


FIG. 3. (Color online) Evolution of the DOS with different U/t values for neutral C_{20} isomers: cage, bowl and ring. $U/t=5$ for cage isomer is from exact diagonalization (Ref. 11). Others are from QMC simulations. Fermi energies are located at $\omega=0$.

fective one-band Hubbard model [Eq. (1)] to account for the electron correlations. To perform such a study of on-site electronic correlation on the C_{20} isomers we use the standard QMC algorithm.^{17–19} In regimes where the sign problem in this approach renders results unobtainable, we supplemented these results by exact diagonalization (ED) results. This allows us to determine the DOS as a function of U/t . The DOS is calculated for each of the neutral isomers for $U/t = 2, 3, 4, 5$. Our results are shown in Fig. 3. As expected, the energy gap increases with increasing U/t values for the bowl and the ring. The dependence on U/t is clearly nontrivial. For the fullerene cage the initially metallic molecule becomes insulated with increasing $(U/t)_{\text{cage}}$. For molecular solids formed out of this isomer a metal-insulator transition is therefore expected around $(U/t)_{\text{cage}}=4.1$.¹¹

In Sec. V we estimate the on-site Coulomb interaction U using the affinity energy of the isomers. However, assuming that the on-site electronic energy scale is $U \sim 10$ eV for all the isomers,^{20–23} we can do a rough estimate of U/t and hence estimate the gap for the neutral molecule from the above QMC results for the DOS. Using this value for U we find that $U/t \sim 4.2, 3.2$ for the bowl and ring isomers, respectively, using $t_{\text{ring}} \approx 3.16$ eV and the upper bound $t_{\text{bowl}} \approx 2.36$ eV. For these values of U/t and from Fig. 3, we estimate energy gaps for the neutral bowl and ring isomers to be about $\Delta_{\text{bowl}}=2.0t_{\text{bowl}}=4.72$ eV and $\Delta_{\text{ring}}=0.9t_{\text{ring}}=2.73$ eV, respectively. For the cage isomer $(U/t)_{\text{cage}}$ should

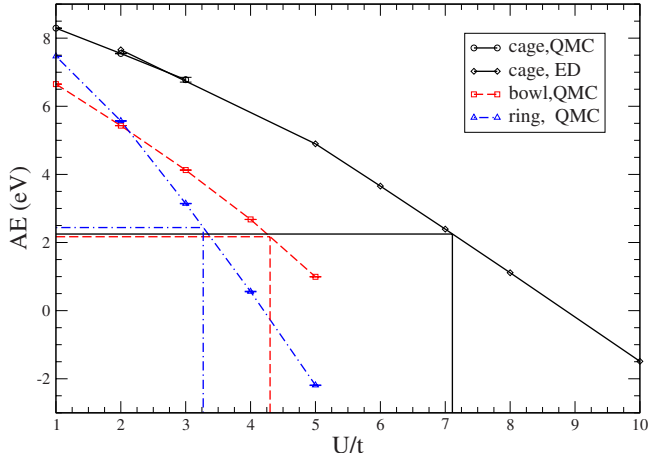


FIG. 4. (Color online) Variation in affinity energy with U/t for the C_{20} cage, bowl, and ring from QMC and ED calculations. The experimental AE values are shown by the horizontal lines intercepting the $AE \sim U/t$ curves. The corresponding U/t values are shown by the vertical lines intercepting the curves. Results are shown using the upper bound for t for the cage and bowl.

be around 7, using the upper bound $t_{\text{cage}}=1.36$ eV. Unfortunately, the sign problem prevents us from calculating the DOS and hence the gap by QMC simulations for $(U/t)_{\text{cage}} > 3$, and we have to resort to the much more time consuming ED approach. Previously, using ED techniques, the DOS and gap at $(U/t)_{\text{cage}}=5$ have been determined,¹¹ yielding a gap of 1.89 eV. (see Fig. 3). We have repeated this calculation at $(U/t)_{\text{cage}}=10$, finding a gap of 7.67 eV. Linearly interpolating between these values we estimate the gap for the fullerene cage at $(U/t)_{\text{cage}} \sim 7$ to be $\Delta_{\text{cage}}=3.1t_{\text{cage}}=4.2$ eV.

V. ESTIMATE OF THE ON-SITE INTERACTION, U/t

Electron correlations are important for an accurate calculation of the affinity energy, as shown by early QMC simulations (see, e.g., Ref. 24). Therefore, starting from the affinity energy, one can use QMC simulations to determine electron correlations, which in the case of Hubbard model are represented by the on-site interaction U . Since the electron affinity energies, AE, were measured experimentally,¹ we can use these energies for a more refined estimate of the value of the on-site effective Coulomb interaction U for each of the isomers. Ground state energies of the isomers are calculated with projection QMC technique¹⁸ in the Hilbert space of fixed particle number N and magnetization and converted to electron volts using the previously determined estimates for t . The affinity energy $AE=E(20)-E(21)$ is then subtracted and shown in Fig. 4 as a function of U/t . Results are shown using the upper bound for t for the cage and bowl. The sign problem prevents us from simulating larger U/t values with QMC. Instead we use ED to obtain a series of AE for $U/t=2,5,6,7,8,10$ for the cage isomer. Note that for the fullerene cage the electron affinity changes slope around the expected critical value of $(U/t)_{\text{cage}}=4.1$.¹¹ We see that all three curves are approximately linear around the experimental affinity energy values¹ ($AE_{\text{cage}}=2.25$ eV,

TABLE II. Hopping t and on-site Coulomb interaction U for C_{20} isomers: cage, bowl, and ring.

	t (eV)	U (eV)	U/t
Cage	0.68–1.36	8.3–9.67	7.1–12.2
Bowl	2.06–2.36	10.09–10.15	4.30–4.9
Ring	3.16	10.33	3.27

$AE_{\text{bowl}}=2.17$ eV, and $AE_{\text{ring}}=2.44$ eV). Thus, a linear interpolation gives $U_{\text{cage}}=7.1t_{\text{cage}}$, $U_{\text{bowl}}=4.30t_{\text{bowl}}$, and $U_{\text{ring}}=3.27t_{\text{ring}}$. If we, for the fullerene cage, perform a similar analysis using $t_{\text{cage}}^{\text{min}}=0.68$ eV we find instead an even larger value for $(U/t)_{\text{cage}} \approx 12.2$. Likewise, we find for the bowl using $t_{\text{bowl}}^{\text{min}}=2.06$ eV, a value of $(U/t)_{\text{bowl}}=4.9$.

The above results (Fig. 4) show that for cage, bowl, and ring isomers the on-site Coulomb interaction energies are $U_{\text{cage}}=7.1t_{\text{cage}}=9.67$ eV, $U_{\text{bowl}}=4.30t_{\text{bowl}}=10.15$ eV, and $U_{\text{ring}}=3.27t_{\text{ring}}=10.33$ eV, all of which are reasonably close to 10 eV, i.e., the value that was used in Sec. IV. The variation in U/t between the isomers is minor, and the consistency between these results and those of Sec. IV supports our approach of determining t from DFT calculations. Using the upper bounds on U/t for the cage and the bowl with the associated minimal values for the hopping integrals results in $U=8.3$ and $U=10.09$ eV, respectively. It is noteworthy that the value of $(U/t)_{\text{cage}}$ is clearly beyond the metal-insulator transition point $U/t=4.1$ predicted in Ref. 11. This suggests that undoped molecular solids formed with dodecahedral C_{20} are insulators, and the isolated molecule is likely not Jahn-Teller active.¹¹

In conclusion, the estimation of U/t using the molecular affinity energy in combination with a determination of the hopping integral t from DFT is a reasonable approach for the cage, bowl, and ring isomers. We summarize all the isomer parameters in Table II.

VI. ENERGY GAPS AND EFFECT OF ELECTRON DOPING

We proceed to study the effect of one-electron doping on the single-particle excitation spectra of C_{20} bowl and ring isomers with QMC simulations using the hopping integrals $t_{\text{bowl}} \approx 2.36$ eV and $t_{\text{ring}}=3.16$ eV and on-site Coulomb interaction strength U estimated above. A similar study of the fullerene cage would require time consuming ED calculations, which we have not performed. The DOS are shown in Fig. 5. We see that with one-electron doping, spectral peaks for both bowl and ring move toward Fermi levels. Clearly, the one-electron-doped bowl becomes metallic. For the one-electron-doped ring, the spectral weight is very close to the Fermi energy. However, within the precision of the QMC results, we expect the doped ring to remain an insulator with a gap $\Delta_{\text{ring}}^{\text{QMC}}=3.2$ eV. This is in contrast to DFT energy levels (Table I), which show that with one-electron doping both the bowl and the ring isomers become metallic.

From these figures we can also estimate the energy gaps for the neutral bowl and ring to be around $\Delta_{\text{bowl}}^{\text{QMC}}=4.0$ eV

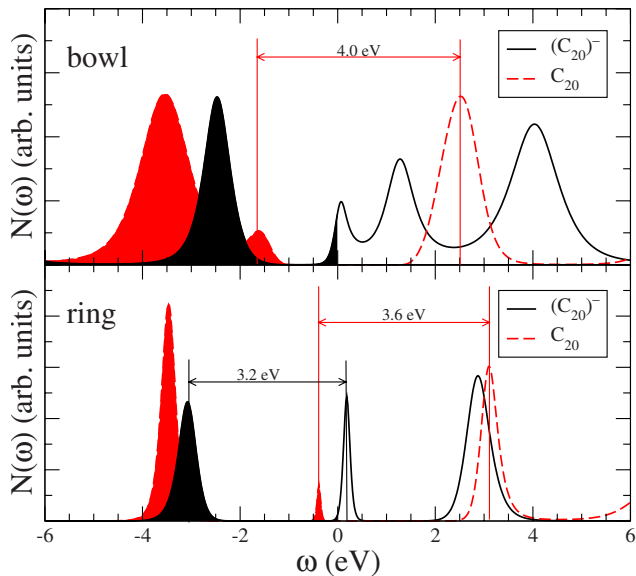


FIG. 5. (Color online) QMC results for the DOS of one-electron-doped C_{20} (solid lines) compared with the neutral molecules (dashed lines). For the bowl, $(U/t)_{\text{bowl}}=4.30$; for the ring, $(U/t)_{\text{ring}}=3.27$. Shaded areas are occupied by electrons. Fermi energies are located at $\omega=0$. Energy units have been converted to eV using $t_{\text{bowl}}=2.36$ eV and $t_{\text{ring}}=3.16$ eV, respectively. Energy gaps for the neutral molecules and doped ring are shown in the figure.

and $\Delta_{\text{ring}}^{\text{QMC}}=3.6$ eV in reasonable agreement with the rough estimate given in Sec. IV. We note that these values are much larger than the corresponding DFT values $\Delta_{\text{bowl}}^{\text{DFT}}=2.4$ eV and $\Delta_{\text{ring}}^{\text{DFT}}=1.4$ eV. From the above discussion we expect our previous estimate of the gap for the fullerene cage of $\Delta_{\text{cage}}=3.1t_{\text{cage}}=4.2$ eV at $(U/t)_{\text{cage}}\sim 7$ to be relatively precise. Hopefully, these estimates of the gaps can be compared to future experimental PES and inverse PES of the neutral C_{20} isomers.

VII. CONCLUSIONS

We proposed an effective Hamiltonian approach to study the electronic correlations in C_{20} isomers with QMC simulations and exact diagonalization. The hopping integral, t , in an effective one-band Hubbard model Hamiltonian is determined by comparing DFT energy levels with the tight-binding Huckel energy levels. On-site Coulomb interactions, U , are then determined by comparison to the experimental affinity energies of the isomers. With these estimated parameters, QMC calculations of the resulting effective Hubbard model then predict insulating behavior of the neutral (cage, bowl, and ring) and one-electron-doped (ring) isomers and metallic behavior of the one-electron-doped bowl isomer. We find qualitative agreement between QMC and DFT calculations for neutral (bowl and ring) isomers and one-electron-doped bowl isomer, although QMC gives much larger energy gaps for the neutral isomers. For the neutral cage isomer, the QMC prediction (insulating) is qualitatively different from DFT calculations (metallic) since the cage C_{20} is the most strongly correlated molecule of the three isomers with a ratio of on-site Coulomb interaction and hopping integral of $(U/t)_{\text{cage}}\approx 7.1-12.2$ exceeding the value of 4.1 for the predicted metal-insulator transition. Results presented in the paper await a comparison with possible future PES and inverse PES experiments on the gas phase of C_{20} isomers.

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