Strong correlation effects in the fullerene \( \text{C}_{20} \) studied using a one-band Hubbard model

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The smallest fullerene, dodecahedral \( \text{C}_{20} \), is studied using a one-band Hubbard model parametrized by \( U/t \). Results are obtained using exact diagonalization of matrices with linear dimensions as large as \( 5.7 \times 10^9 \), supplemented by quantum Monte Carlo. We report the magnetic and spectral properties of \( \text{C}_{20} \) as a function of \( U/t \) and investigate electronic pair binding. Solid forms of \( \text{C}_{20} \) are studied using cluster perturbation theory, and evidence is found for a metal-insulator transition at \( U \sim 4t \). We also investigate the relevance of strong correlations to the Jahn-Teller effect in \( \text{C}_{20} \).

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The smallest fullerene, \( \text{C}_{20} \), contains 12 carbon pentagons (and no hexagons) forming a dodecahedron in a perfect representation of a platonic solid. Among the many possible isomers of \( \text{C}_{20} \), it is not obvious that this dodecahedral fullerene cage should be the most stable, and theoretical studies\(^1,2\) have reached different conclusions. In addition, unlike \( \text{C}_{60} \), dodecahedral \( \text{C}_{20} \) is not spontaneously formed in condensation or cluster annealing processes,\(^3\) and its extreme curvature and strong reactivity led to doubts about its stability. It therefore created considerable excitement when Prinzbach et al.\(^4\) succeeded in producing the dodecahedral fullerene isomer of \( \text{C}_{20} \) in the gas phase. Experiments have also shown evidence for solid phases of \( \text{C}_{20} \),\(^5,6\) although the crystal structure is still debated. Density-functional studies of the solid forms of \( \text{C}_{20} \) (Refs. 6–10) have suggested different crystal structures with the most promising candidate, \( \text{C}_{20} \) cages connected by C atoms to form a 22 atom unit cell,\(^6,9\) predicted to become superconducting upon doping with Na.\(^9\) A simple-cubic-like phase of \( \text{C}_{20} \) has also been speculated to become superconducting.\(^8\) In their proposal for a purely electronic mechanism for superconductivity in \( \text{C}_{60} \), Chakravarty et al.\(^11\) have stressed the importance of structure at the mesoscale.\(^12\) Along with the molecular solids formed by \( \text{C}_{60} \), solid phases of \( \text{C}_{20} \) would be ideal candidates for this picture, and a detailed understanding of these phases would be of great interest. Strong correlation effects are likely to be important in \( \text{C}_{20} \), and previous studies\(^1,2,6,7,9,10,13\) have treated these correlation effects approximately. Here, we show that within a Hubbard model description, an almost exact treatment is possible using a large-scale numerical approach. Our starting point is the one-band Hubbard Hamiltonian on a single \( \text{C}_{20} \) molecule defined as:

\[
H = -t \sum_{\langle ij \rangle \sigma} (c^\dagger_{i \sigma} c_{j \sigma} + \text{H.c.}) + U \sum_i n_{i \uparrow} n_{i \downarrow},
\]

where \( c^\dagger_{i \sigma} \) \( (c_{i \sigma}) \) is an electron creation (annihilation) operator, \( U \) is the on-site Coulomb interaction, and \( n_{i \sigma} \) is the number of electrons on site \( i \) with spin \( \sigma \). Due to the extreme curvature of \( \text{C}_{20} \), we expect \( t \) to remain smaller than typical values for \( \text{C}_{60} \) while \( U \) should remain close to that of \( \text{C}_{60} \). Consequently, we expect that a realistic value for \( U/t \) valid for \( \text{C}_{20} \) is likely larger than the value of \( U/t \sim 4 \) (Ref. 14) used for \( \text{C}_{60} \), implying that strong correlation effects play a more crucial role in the physics of \( \text{C}_{20} \). The Hamiltonian, Eq. (1), is a simplified model of \( \text{C}_{20} \) and our use of this model is motivated by two distinct rationales. First, this model is of central importance in the theory of strongly correlated electronic systems. The \( \text{C}_{20} \) structure allows us to study strong correlation effects in a relatively large system using exact numerical methods. Second, from earlier work on \( \text{C}_{60} \) molecules, we have found that many features, such as the dependence of extended x-ray-absorption fine structure spectra on molecular orientation, are equally well modeled by detailed local-density approximation (LDA)-type calculations\(^15\) as by quantum Monte Carlo (QMC) simulations of the Hubbard model.\(^14\) On the other hand, it is well established that the Hubbard model provides a more realistic treatment of systems close to a metal-insulator transition. The magnetic metal to nonmagnetic insulator transition that we find for increasing \( U \) (see below) would be difficult to model in LDA.

Even though \( \text{C}_{60} \) and \( \text{C}_{20} \) share the same symmetry group, \( I_h \), noninteracting \( \text{C}_{20} \) is a metal while neutral \( \text{C}_{60} \) is an insulator. This is evident from the Hückel molecular orbitals (HMOs) shown in Fig. 1(a). The highest occupied molecular orbital \( G_a \) is fourfold degenerate, containing two electrons for the neutral molecule. The lowest unoccupied molecular orbital \( G_\sigma \) is considerably higher in energy. To simplify the problem, we shall mainly be concerned with neutral, one- and two-electron doped molecules which only involves the \( G_a \) levels.

Due to the orbital degeneracy of the neutral \( \text{C}_{20} \) molecule, the Jahn-Teller effect is expected to be important. The electronic \( G_a \) levels can couple to the \( A_v \), \( G_\sigma \), and \( H_g \) Jahn-Teller phonon modes. We focus exclusively on the effects of a static distortion. The inclusion of dynamic phonons in our model would be highly interesting but is not possible within our exact diagonalization approach. Theoretical studies have argued for the resulting lowered symmetry to be \( \text{C}_{20} \),\(^16\) \( D_{5d} \),\(^17\) \( C_{2v} \),\(^18\) \( C_{1v} \),\(^19\) and \( D_{3d} \).\(^20\) Here, we follow Yamamoto et al.\(^20\) and assume a static deformation of \( D_{3d} \) symmetry. The bond lengths for the optimal \( D_{3d} \) structure are\(^20\) \( a_{d_{h}} = 1.464 \text{ Å} \), \( b_{d_{e}} = 1.469 \text{ Å} \), \( a_{d_{v}} = 1.519 \text{ Å} \), and \( a_{d_{c}} = 1.435 \text{ Å} \). (See Fig. 1 of Ref. 20.) We parametrize the distortion by letting \( t_{d_n} \), the hopping along the bond of length \( a \), depend on a parameter \( \varepsilon \) in the following way: \( t_{n}/t=1-\varepsilon (a-a)/a \). Here, \( a \)
time of each Lanczos step is dominated by computation rather than communication and scales nearly linearly with \( P \). For \( P=64 \), a Lanczos iteration for the \( I_0 \) \((D_{3d})\) configuration is completed in 540 (980) s. 21 Dynamical properties are calculated using standard ED techniques. 22 Our quantum Monte Carlo (QMC) follows standard methods 23 with ground-state energies obtained from projector QMC, while spectral functions are obtained from finite temperature, \( \beta=10/t \), QMC 23 combined with maximum entropy methods. 24

**Magnetic properties.** From the noninteracting HMO levels in Fig. 1, it would appear that the ground state of the neutral molecule is magnetic at small \( U/t \). Our ED and QMC work confirms that this is the case for the \( I_0 \) configuration for \( U/t \leq 3 \), where the ground state is observed to be an orbitally degenerate triplet, \( S=1 \), occurring at \( j_{10}=0, \pm 2 \). Table I gives the few lowest energy levels, labeled by spin and pseudoangular momentum, for the cases of \( U/t=2 \) and 5. For \( U/t \geq 5 \), we find that the ground state for the \( I_0 \) configuration is a nondegenerate singlet, \( S=0 \), occurring at \( j_{10}=5 \), and separated from the lowest-lying excitation, another singlet at \( j_{10}=0, \pm 2, \pm 4 \), by a gap of 0.7. The lowest triplet excitation is found at \( j_{10}=0, \pm 2, \pm 4 \). This ordering of levels continues to hold for larger \( U/t \), although the energy scale decreases with increasing \( U \). The degeneracies and excitation gaps at large \( U/t \) agree with ED studies of the dodecahedral \( S=1/2 \) antiferromagnetic Heisenberg model. 25 In fact, the ground-state energy calculated for neutral \( C_{20} \) in the large \( U \) limit (\( U>50 \)) can be related to the ED result for the Heisenberg model to the accuracy that the latter has been calculated. 26

From Table I, it is clear that the system crosses over from a triplet to singlet ground state between \( U/t=2 \) and \( U/t=5 \). Assuming a linear dependence on \( U/t \) of the energy of the triplet states at \( j_{10}=0, \pm 2 \) and the singlet at \( j_{10}=5 \), we estimate that this transition occurs at \( U/t \approx 4.10 \), indicated by the solid vertical line in Fig. 2. The fact that the ground state for the neutral molecule for \( U>U_c \) is a nondegenerate singlet implies that the molecule is stable against Jahn-Teller distortions for large \( U \).

Surprisingly, the \( D_{3d} \) distorted molecule follows the same pattern with the exception that at \( U/t=0 \), the unique ground state is a singlet. However, once \( U/t \) becomes of order of the splitting of the \( G_u \) levels, \( \sim 0.0686 \), the ground state becomes a triplet. At \( U/t=0.5 \) and 2, we find that this ground state triplet occurs at \( j_6=0 \) with a number of low-lying triplet

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**TABLE I.** Lowest energy levels (in units of \( t \)) of the neutral \( C_{20} \) molecule for \( U=2t, 5t \), labeled by spin and pseudoangular momentum, for the \( I_0 \) \((j_{10})\) and \( D_{3d} \) \((j=j_6)\) configurations.

<table>
<thead>
<tr>
<th>( j )</th>
<th>( S )</th>
<th>( U=2t )</th>
<th>( U=5t )</th>
<th>( j )</th>
<th>( S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_0 )</td>
<td>-20.5983834340</td>
<td>1</td>
<td>0, \pm 2</td>
<td>-20.112842959</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>-20.5981592741</td>
<td>1</td>
<td>0, \pm 4</td>
<td>-12.0123014488</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>-20.5920234655</td>
<td>0</td>
<td>0, \pm 2, \pm 4</td>
<td>-11.6770332831</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>-20.0527029539</td>
<td>0</td>
<td>5</td>
<td>-11.8472120431</td>
<td>1</td>
</tr>
<tr>
<td>( D_{3d} )</td>
<td>-20.6757641960</td>
<td>1</td>
<td>0</td>
<td>-12.1204684092</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>-20.64625357924</td>
<td>1</td>
<td>\pm 2</td>
<td>-12.0921677742</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>-20.616698560</td>
<td>0</td>
<td>\pm 2</td>
<td>-11.9197052918</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>-20.0754248172</td>
<td>0</td>
<td>3</td>
<td>-11.8974914914</td>
<td>1</td>
</tr>
</tbody>
</table>
FIG. 2. (Color online) Electronic pair binding energy $\Delta_b(21)/t$ as a function of $U/t$. ED (●) and QMC (○) results for the molecule with $I_h$ symmetry. ED results ($\blacktriangle$) for the molecule with $D_{3d}$ ($e = 1$) symmetry. The solid (crossed) vertical line indicates $U_c/t$ for neutral $I_h$ ($D_{3d}$) molecules. (a) $\Delta_b$ versus $U/t$ for $U/t \leq 5$. (b) $\Delta_b$ versus $t/U$ for $5 \leq U/t \leq 100$.

states above it. The Jahn-Teller distortion has therefore completely removed the orbital degeneracy leaving only a Kramer’s degeneracy. At $U/t = 2$, the lowest-lying excitation is a triplet at $j_b = \pm 2$, and the lowest-lying singlet, with a gap approximately twice as large, is at the same $j_b = \pm 2$. As for the $I_h$ configuration, we observe that the ground state is a singlet at $U/t = 5$ occurring at $j_b = 3$. An analysis similar to the $I_h$ case yields $U_c/t \approx 4.19$, indicated by the crossed vertical line in Fig. 2, very close to the estimate for the $I_h$ configuration. Again, the system remains in a singlet state for larger values of $U/t$.

Pair binding. The purely electronic mechanism for superconductivity is based on a favorable pair binding energy. The pair binding energy is defined as the energy difference between having two electrons on the same and on separate molecules:

$$\Delta_b(N + 1) = E(N + 2) - 2E(N + 1) + E(N).$$

When negative, it is favorable to have the two electrons on the same molecule providing a purely electronic mechanism for superconductivity. Intriguingly, for neutral C$_{22}$, as well as for several related models, it is known that $\Delta_b$ is negative. For C$_{60}$, perturbative results indicated that the observed superconducting phase has its origins in a negative $\Delta_b$. However, earlier QMC results find no binding, suggesting that either low order perturbation theory is inadequate or that the QMC results are not sufficiently accurate to measure the binding. Thus, it is of considerable interest to obtain exact results for C$_{20}$ which can then be used to test the accuracy of QMC.

Our results for $\Delta_b(21)/t$ are shown in Fig. 2. We first consider results for the $I_h$ configuration of C$_{20}$. The QMC results (○) and the ED results (●) are in excellent agreement, and for $U/t \leq 3$, they show that $\Delta_b$ is positive and pair binding is suppressed. (For $U > U_c$, it is not possible to perform QMC calculations due to the sign problem.) The ground state for the neutral molecule is now a singlet and our ED results again clearly indicate that pair binding is not favored. As $U/t$ increases, $\Delta_b$ reaches a minimum at $U/t \approx 10$. Then, as $U/t \to \infty$, $\Delta_b$ approaches a finite positive value, consistent with the exact result showing the absence of pair binding for electron doping in the $U \to \infty$ limit.

We can only calculate the pair binding for the Jahn-Teller distorted molecule in an approximate manner since the distortion will depend on the electron doping. We make the simplifying assumption that the distortion is static, of $D_{3d}$ symmetry, and independent of doping. We find that the Jahn-Teller distortion makes pair binding less favorable. We have also investigated the effects of nearest neighbor repulsion $V$ in an extended Hubbard model and find that it too works against pair binding. An important difference between the ground states for small and large $U$ is the relative stability of the gapped state for $U > U_c$ against the Jahn-Teller distortion. In Fig. 3, we show results for the shift in the ground-state energy versus $\epsilon$ where the strong dependence on $\epsilon$ for $U/t = 2$ is indicative of the molecule being Jahn-Teller active. By

FIG. 3. (Color online) Shift in the ground-state energy of the neutral molecule, $\Delta E$, versus the distortion $\epsilon$. The Jahn-Teller instability is quite pronounced for $U/t = 2$ (○), but it is essentially absent for $U/t = 8$ (●).

FIG. 4. (Color online) Density of states $N(\omega)$ at (a) $U = 2t$ from QMC and at (b) $U = 5t$ from ED. In both panels, the density of states for the C$_{22}$ fcc lattice obtained from CPT with $t' = -t$ is shown as a dashed line.
contrast, for $U/t=8$, the dependence on $\varepsilon$ is very shallow, signaling that the $I_h$ structure is stable.

**Spectral functions and solid C$_{20}$.** Next we calculate the density of states $N(\omega)$ and wave-vector dependent spectral functions $A(k,\omega)=-\langle i\omega \rangle \text{Im}[G(k,\omega+E_0+i\eta)]$ for a three-dimensional solid of C$_{20}$ molecules. Here, $E_0$ is the ground-state energy and $G$ the single-particle Green’s function. The calculation is performed by cluster perturbation theory (CPT) using QMC and ED data. In all cases, delta functions were treated as Lorentzians with a broadening of $\eta=0.1$. The QMC version of this method was applied earlier to the case of C$_{60}$ monolayers. We idealize the hypothetical fcc C$_{22}$ structure by a model in which the bridging C atoms are replaced by effective hopping integrals, $t'$, which lies in the middle of the region of triplet ground state, the solid of undistorted $I_h$ molecules is metallic with a complicated Fermi surface, while, for $U/t=5$, in the region of singlet ground state, the solid is insulating with a gap of about 1.4$t$ and some narrowing of the “bands” close the Fermi energy is observed.

In conclusion, we have calculated the ground-state properties and spectral functions of the Hubbard model on a C$_{20}$ molecule using ED and QMC and have shown that pair binding is not favored in this molecule. We have identified a distortion to a gapped singlet state which is stable. Extending this result using CPT, we identify a metal-insulator transition for the bulk solid at $U=U_c$. If the symmetric, $I_h$, form of C$_{20}$ is found to be stable, a possible explanation would be that it is stabilized by correlations resulting from $U>U_c$.

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\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig5.pdf}
\caption{Spectral functions with the chemical potential $\mu$ determined from $N(\omega)$ in Fig. 4. Results for the C$_{22}$ fcc lattice with (a) $U=2t$ and (b) $U=5t$ as obtained from CPT with $t'=-t$. The k-axis labels refer to standard notation for the FCC Brillouin zone.}
\end{figure}


26. For large $U/t$, the neutral molecule ground-state energy can be fitted to $E_N/t^2(U)=a+b(t/U)^2$, where $a=4E_gJ^2+30$ and $E_g$ is the ground-state energy of the Heisenberg model, obtained by exact diagonalization in Ref. 25, $E_H=-9.722 19J$. A fit, using ED results for $U/t=50$ and 100, gives $E_{H}=-9.722 17J$.