VARIATIONAL MONTE CARLO AND CONFIGURATION INTERACTION STUDIES OF $C_{60}$ AND ITS FRAGMENTS

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Abstract

The $C_{60}$ molecule and its fragments are studied using Configuration Interac-
tion (CI) and Variational Monte Carlo (VMC) techniques, within the Hubbard
model. Using benzene as a test case, we compare the results of the approxi-
mate calculations with exact calculations. The fragments of $C_{60}$ studied are
pyracylene, fluoranthene and corannulene. The energies, bond orders, spin–
spin and charge–correlation functions of these systems are obtained for various
values of the Hubbard parameter, $U$. The analysis of bond orders and corre-
lation functions of these individual molecules allow us to visualise pyracylene
as a naphthalene unit with two ethylenic moieties and fluoranthene as weakly
bridged benzene and naphthalene units. Corannulene is the largest fragment of
$C_{60}$ that we have studied. The hexagon–hexagon(h–h) bond orders are slightly
larger than those of the hexagon–pentagon bonds(h–p), a feature also found in
other fragments. We also find bonds between two coordinated carbon sites to
be stronger than bonds involving three coordinated carbon sites. In $C_{60}$, the
h–h bonds are stronger than in corannulene and the h–p bonds weaker than
in corannulene for all correlation strengths. Introducing bond alternation in
the buckyball enhances this difference.
1 Introduction

The discovery of $C_{60}$, a new allotrope of carbon, by Kroto et al[1] and its bulk synthesis by Kratschmer et al[2] have been amongst the most exciting recent developments in chemistry and physics. $C_{60}$ and its compounds show exotic physical and chemical properties. Alkali doped compounds of $C_{60}$ are superconducting, with $Rb_{1.5}Cs_{1.5}C_{60}$ having a superconducting transition temperature of 32 K[3]. The compound $C_{60} - TDAE$ ($TDAE$=tetrakis dimethyl amino ethylene) is an organic ferromagnet with a fairly large Curie temperature of 16.5K[4, 5].

To develop models for diverse phenomena such as these, it is essential to have a reliable understanding of the electronic structure of the basic building blocks of these systems. The carbon atoms in fullerenes are in a nearly $sp^2$ hybrid configuration with a half–filled $p_{\pi}$–like orbital directed radially and involved in extended conjugation. Electronic structure studies on conjugated organic systems have brought out clearly the importance of electron correlations to account for many of the observed spectroscopic and related properties[6]. Explicitly including electron correlations is a formidable challenge even at the level of a single buckyball. It is reasonable to hope that a proper study of a single buckyball and its fragments will shed light on the esoteric electronic properties of these systems in the bulk.

It would be interesting to try and understand the properties of the full buckyball in terms of its fragments. Firstly, for small enough fragments, it is
possible to perform exact calculations that allow us to systematically check the approximate methods. The electronic structures of the fragments are expected to be useful in interpreting the electronic structure and geometry of $C_{60}$. In this article, we study the ground state properties such as bond orders, charge–charge and spin–spin correlation functions of some fragments of $C_{60}$ using configuration interaction (CI) techniques and the Variational Monte Carlo (VMC) method. We report the results of our VMC calculations on the full buckyball within the Hubbard model, with and without bond-alternation.

The simplest description of the electronic structure of $C_{60}$ is found within the framework of the Huckel picture, wherein a non-zero transfer integral is introduced between the $p_{\pi}$–like orbitals on nearest–neighbour atoms(sites). The resulting molecular orbitals (MOs) have a high degree of degeneracy due to the icosahedral symmetry of the molecule. Neutral $C_{60}$ has a five-fold degenerate set of highest occupied molecular orbitals (HOMOs) and a three-fold degenerate set of lowest unoccupied molecular orbitals (LUMOs). The high degeneracy of the MOs has been the focal point of the discussion of the electronic structure of these systems. For instance, in a first approximation, the degeneracy of the LUMOs is considered essential to rationalize the existence of ferromagnetic exchange between two monoanions of $C_{60}$[7].

The minimal interacting description for $C_{60}$ is given by the single band Hubbard model which incorporates only an on-site electron–electron repulsion $U$ besides the one-electron part given by the Huckel picture. Drastic truncation of the electron repulsion to an on–site interaction is justifiable in a metal where
the mobile conduction electrons lead to short Debye–Huckel screening lengths. In molecules it is strictly necessary to include extended range interactions, at least at the level of the PPP model, because of inefficient screening. However, obtaining reliable results even for such models is difficult and we study the simpler Hubbard model as a first step in understanding crucial qualitative effects of correlations in molecular systems like $C_{60}$ and its fragments. Exact diagonalization techniques are useful for small systems (with less than about 14 sites at present) but are impractical for large systems because of the exploding dimension of the basis with increasing system size. Therefore, approximate approaches to the problem are inescapable for larger systems. However, exact diagonalization provides a strong check on any novel approximation scheme.

Amongst approximate techniques, perturbation theory gives fairly reliable results at limiting values of the model parameters but breaks down for intermediate but relevant values of the parameters. Another equally widely used approximate approach has been the variational approach with the Gutzwiller wavefunction (GWF) as the trial function of choice for Hubbard models. In this approach, a variational parameter $g$ ($0 \leq g \leq 1$) is introduced and the weight of a configuration in the site representation of the Hartree–Fock ground state is modified by a factor $g^D$, where $D$ is the number of double occupancies in that configuration. Even though a single variational parameter ($g$) is to be determined, the method itself is not easy to implement. Evaluation of the expectation value of the Hamiltonian for the GWF is made difficult by the very large number of configurations appearing in the wavefunction in the site
representation. Often, uncontrolled approximations are resorted to for evaluating the expectation value\cite{10, 11}. Such approximations can be avoided if we carry out a Monte Carlo integration for the expectation value, using the VMC method. The VMC technique uses an importance sampling of the various Slater Determinants (in the atomic orbital (AO) basis) that make up the Gutzwiller trial function to estimate the expectation value of the Hamiltonian.

We also employ a novel configuration interaction (CI) technique that considers all many-body states derived from multiple particle–hole excitations from the Hartree-Fock ground state, whose one particle energies lie below a chosen cutoff. The technique gives reliable ground and excited states of small fragments of $C_{60}$ for comparison with Monte Carlo studies. We carry out VMC studies on the full buckyball using the optimized Monte Carlo parameters arrived at from such comparisons.

This article is organized as follows. In the next section we give a description of the computational schemes we have employed, namely the approximate CI scheme and the VMC method employing Gutzwiller trial function. We provide detailed comparisons of these techniques with exact results for benzene. Section 3 deals with our results and discussions on fragments of $C_{60}$. In section 4 we discuss our VMC results on $C_{60}$ and compare these with results on fragments. The last section summarizes the main results of the paper.
2 Computational Schemes

The computational schemes that are described in this section are applied to the Hubbard model \[12\] on the buckyball and its fragments. The Hubbard Hamiltonian may be written as

\[
H_{\text{Hub}} = H_0 + H_1
\]

\[
H_0 = \sum_{<ij>} \sum_\sigma t_{ij} (a_{i\sigma}^{\dagger} a_{j\sigma} + a_{j\sigma}^{\dagger} a_{i\sigma})
\]

\[
H_1 = U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}
\]

where \(H_0\) is the non-interacting part of the Hamiltonian and \(H_1\) represents the on-site Coulomb repulsion. The operator \(a_{i\sigma}^{\dagger}\) \((a_{i\sigma})\) creates (annihilates) an electron with spin \(\sigma\) in the orbital at the \(i\)th site, \(\hat{n}_{i\sigma}\) are the corresponding number operators and the summation \(<ij>\) is over bonded atom pairs. The transfer integral in all the computations is fixed at 1.0 and energies are reported in units of \(t\) unless specified otherwise.

2.1 VB Method in the MO Basis

In carrying out approximate electronic structure calculations of large systems, within a restricted CI scheme, it is important to find a criterion for truncating the basis. In general, it is difficult to find a truncation scheme to restrict the size of the Hilbert space, that yields accurate spectral gaps. The crux of the problem is that increasing the dimensionality of the basis set in the restricted CI scheme undoubtedly improves the ground state energy in accordance with
the variational theorem, but does not guarantee a concommitant improvement in the excited state energies. The scheme described here is intuitive and does not have the drawback of the uncontrolled nature of the multi-reference CI (MRCI) schemes in which the MOs chosen in the reference determinants are arbitrary\[13\].

In our restricted CI scheme, we employ the MOs to construct the VB functions\[14\]. The Hubbard Hamiltonian in the MO basis can be written as

$$ H = \sum_{p\sigma} \epsilon_p b_{p\sigma}^\dagger b_{p\sigma} + 1/2 \sum_{pqrs} W_{pqrs} (\hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps}) $$

$$ \hat{E}_{pq} = \sum_{\sigma} b_{p\sigma}^\dagger b_{q\sigma} $$

where $b_{p\sigma}^\dagger$ ($b_{p\sigma}$) corresponds to creation (annihilation) of an electron in the $p^{th}$ molecular orbital with spin $\sigma$, $\epsilon_p$ is the energy of the $p^{th}$ MO. $W_{pqrs}$ is defined by

$$ W_{pqrs} = U \sum_i c_{ip} c_{iq} c_{ir} c_{is} $$

where $c_{ip}$ is the coefficient of the $i^{th}$ AO in an AO expansion of the $p^{th}$ MO and all the summations run over the entire respective bases. The Hubbard Hamiltonian written in the MO basis has the property that the one-electron part is diagonal, while the interaction part is off-diagonal. We use the Rumer-Pauling\[15\] rules to construct the VB diagrams from the MOs. However, if an MO state is degenerate, the associated MO functions may not be orthogonal. To avoid the 'nonorthogonality catastrophe', we construct the Lowdin orthogonalized MOs\[16\] whose coefficients are given by

$$ \mathbf{c}^L = \mathbf{S}^{-1/2} \mathbf{c} $$

8
where $S$ is the overlap matrix in the MO basis and $c$ and $c^L$ are the coefficient matrices. We then form the matrix representation of the Hamiltonian in the MO–VB basis using rules similar to those developed for AO–VB calculations [17, 18]. The restricted MO–VB basis includes all configurations whose energy with respect to the energy of the ground state configuration is below a given threshold, $E_c$. We have observed that when $E_c$ equals the spread in the one–particle spectrum (bandwidth of the extended systems), the excitation gaps smoothly follow the exact gaps in small systems. The limitation of this approach arises from the fact that as the system size increases, the Hamiltonian matrix becomes less sparse and this places a restriction on the largest system size accessible by this technique. If we are only interested in the ground state properties of the system, keeping the largest possible cutoff would be appropriate in accordance with the variational principle. We usually keep $E_c \approx$ bandwidth for ground state properties of a single molecule.

### 2.2 Variational Monte Carlo with the Gutzwiller Trial Function

The VMC method employs a trial wavefunction, usually of the Jastrow form [19, 20] and provides a Monte Carlo estimate of the expectation value of the Hamiltonian and other operators in this state for different values of the variational parameters. Here, we focus on the Gutzwiller trial wavefunction which is the simplest Jastrow function and is appropriate for Hubbard models. In this section, we briefly describe our implementation of the VMC method, which is
similar to that of Yokoyama and Shiba\cite{21}.

The Gutzwiller wavefunction is given by

\[ |\Psi_G \rangle = g^{\hat{D}} |\Phi \rangle \]  \hspace{1cm} (8)

\[ \hat{D} = \sum_i \hat{D}_i \]  \hspace{1cm} (9)

\[ \hat{D}_i = n_{i\uparrow} n_{i\downarrow} \]  \hspace{1cm} (10)

where \( g \) is the sole variational parameter. Here \( |\Phi \rangle \) is the ground state, given by,

\[ |\Phi \rangle = |\Phi_{\uparrow} \rangle |\Phi_{\downarrow} \rangle \]  \hspace{1cm} (11)

\[ |\Phi_{\sigma} \rangle = \prod_p b_{p\sigma}^\dagger |0 \rangle \]  \hspace{1cm} (12)

where the product is over the MO’s occupied with electrons of spin \( \sigma \). The state \( |\Phi \rangle \) can be written in terms of the states \( |R \rangle \), where \( |R \rangle = |R_{\uparrow} \rangle |R_{\downarrow} \rangle \) represents a given configuration of up and down spins in real space (equivalently in AO or site representation), as

\[ |\Phi \rangle = \sum_{R_{\uparrow}} \sum_{R_{\downarrow}} det(\mathbf{C}_{\uparrow}(R_{R_{\uparrow}}))det(\mathbf{C}_{\downarrow}(R_{R_{\downarrow}})) |R_{\uparrow} \rangle |R_{\downarrow} \rangle . \]  \hspace{1cm} (13)

Here \( det(\mathbf{C}_{\sigma}(R_{R_{n}})) \) is an \( N_{\uparrow} \times N_{\uparrow} \) determinant whose elements in the \( j \)th row correspond to the coefficients of the \( j \)th occupied MO (for this spin) at the sites occupied in the configuration \( |R_{R_{n}} \rangle \). The operator \( \hat{D} \) picks out the number of doubly occupied sites \( d(R) \) in every configuration \( |R \rangle \) appearing in \( |\Phi \rangle \) (eqn. 13).
In the VMC method, we seek to evaluate the energy expectation value of the Hamiltonian in the state $|\Psi_G>$,

$$E(g) = \frac{<\Psi_G|H|\Psi_G>}{<\Psi_G|\Psi_G>}$$  \hspace{1cm} (14)

To do so, we rewrite $E(g)$ as

$$E(g) = \sum_R P_g(R) \frac{<\Psi_G|H|R>}{<\Psi_G|R>}$$  \hspace{1cm} (15)

where $P_g(R)$ is the probability of occurrence of the configuration $|R>$ given by

$$P_g(R) = \frac{|<R|\Psi_G>|^2}{\sum_{R'}|<R'|\Psi_G>|^2}.$$  \hspace{1cm} (16)

From eqn. (13) for $|\Phi>$, it follows that

$$<R_n|\Psi_G> = g^{d(R_n)}det(C^\dagger(0))det(C^\dagger(R_n)).$$  \hspace{1cm} (17)

A direct importance sampling of the configurations $\{|R>\}$ with weights given by eqn. (16) is not possible since there is an explosion in the number of configurations for large systems and the denominator in eqn. (16) cannot be evaluated explicitly. Therefore, we resort to an indirect importance sampling technique which is achieved by a Markov process. The states of the Markov chain are the configurations and the one-step transition probability between configurations is such as to yield $P_g(R)$ (eqn. (16)) in the ergodic limit. In the computational procedure, we generate the configuration $|R_{n+1}>$ from $|R_n>$ by hopping an electron of randomly chosen spin, from a randomly chosen occupied site, to a randomly chosen vacant site. The new configuration
$|R_{n+1}\rangle$ is accepted with probability

$$p_{n,n+1} = \frac{|<R_{n+1}|\Psi_G>|^2}{|<R_n|\Psi_G>|^2}$$  \hspace{1cm} (18)$$

If the new configuration is not accepted, the configuration $|R_n\rangle$ is itself treated as the new configuration. The ratio $p_{n,n+1}$ is given by

$$p_{n,n+1} = g^{2\delta d} \frac{|\det(C^\dagger(R^\dagger_{n+1}))|^2 |\det(C^\dagger(R^\dagger_n))|^2}{|\det(C^\dagger(C^\uparrow_n))|^2 |\det(C^\dagger(C^\uparrow_{n+1}))|^2}$$  \hspace{1cm} (19)$$

where $\delta d (= d(R_{n+1}) - d(R_n))$ denotes the change in the number of doubly occupied sites brought about by the electron hop. We use the updating algorithm of Ceperley et al.\cite{22} to compute the ratio of determinants appearing in eqn. (19). This involves updating the inverses of the matrices $C^\sigma(R^\sigma)$ which can be carried out in $N^2$ arithmetic operations.\cite{23}

The energy expectation value is computed as a sum of the transfer part and the interaction part. It is trivial to compute the expectation value of the interaction part of the Hamiltonian, because it only involves counting the number of doubly occupied sites in a given state. The effect of the hopping operator $\Delta^\sigma_i$ on a state $|R^\sigma_n\rangle$, that hops an electron from site $i$ is

$$\Delta^\sigma_i |R^\sigma_n\rangle = \sum_j |R^\sigma_{n,i\to j}\rangle$$  \hspace{1cm} (20)$$

where $|R^\sigma_{n,i\to j}\rangle$ denotes a configuration generated from $|R^\sigma_n\rangle$ by hopping an electron of spin $\sigma$ from site $i$ to site $j$. The non–interacting part of the Hamiltonian is the sum of $\Delta^\sigma_i$ over all sites $i$ and spin $\sigma$. Thus, we can write the contribution of the state $|R_n\rangle$ to the total energy expectation value for
the Gutzwiller wavefunction $\Psi_G$ as

$$\frac{\langle \Psi_G | H | R_n \rangle}{\langle \Psi_G | R_n \rangle} = -t \sum_i \sum_\sigma \sum_j \frac{\langle \Psi_G | R_{\sigma,i}^{\sigma,i \rightarrow j} \rangle}{\langle \Psi_G | R_{\sigma}^\sigma \rangle} + UN_d$$

(21)

The calculation of other expectation values is similar to the calculation of energy. In particular, the expectation value of any operator $A$ can be estimated by estimating $\langle \Psi_G | A | R \rangle / \langle \Psi_G | R \rangle$. As before, the averaging is carried out after allowing sufficient number of moves per electron (MPE) to reach the ergodic limit.

The standard deviation in the estimated quantities can be taken as an error estimate in any Monte Carlo procedure. In the estimates of energies and related quantities, this requires computing the expectation value of $H^2$ where $H$ is the Hamiltonian. The number of resultant Slater Determinants when the Hamiltonian acts on a single Slater Determinant is of $O(p)$, where $p$ is the number of transfer terms in the Hamiltonian. In $C_{60}$, $p = 360$ as there are 90 nearest neighbour bonds. Therefore, in the estimation of the expectation value of $H^2$, the number of Slater determinants resulting from the operation of $H^2$ on a single Slater determinant is of $O(p^2)$. Thus, computationally, it is very expensive to estimate the expectation value of $H^2$ and hence the standard deviation. However, small systems are amenable to exact Gutzwiller calculations and we have compared VMC estimates with these results to arrive at a satisfactory number of Monte Carlo steps. The actual scaling of Monte Carlo errors with size of the physical system is not known. In large systems, for some model parameters, we have checked that the Monte Carlo averages obtained
with $10^4$ MPE, after allowing about 2000 MPE for reaching ergodicity, do not change within the significant figures quoted in the tables even upon doubling the sample size.

2.3 Comparison of Approximate and Exact Results for Benzene

We first compare our results from the VMC method with exact calculations in the case of benzene. The calculations on benzene include computation of expectation values obtained from the variation of $g$ in the full Gutzwiller wavefunction and also a Monte Carlo estimate of the same. We refer to the former as the true Gutzwiller value and to the latter as the VMC value. In table(1), we compare the energy from exact–diagonalization with the true Gutzwiller energy and the VMC as a function of the Hubbard parameter, $U$. We observe that even upon increasing $U$, both the true expectation value in the Gutzwiller wavefunction and the MC estimate continue to compare well with the exact energy.

The ground state energy alone is not sufficient for a physical picture of the system and it is essential to have reliable correlation functions. Therefore, we have studied the spin–spin and charge–charge correlation functions using all the techniques mentioned above. In table(2), we present the spin–spin and charge–charge correlation functions obtained from the exact calculation, the true Gutzwiller value and the VMC estimate for weak and intermediate on–site correlation strengths $U$. We observe that the GWF gives a good estimate of
the correlation functions and that the errors in the VMC are not much larger. However, it is worth noting that the Gutzwiller method slightly underestimates the role of correlation as is seen from the higher than exact values of $< n_i n_j >$ and the lower than exact values of $| < s_i s_j > |$ for both $U = 1.0$ and $U = 4.0$. The reduction in charge fluctuations and concommitant increase in spin fluctuations with increase in $U$ is suggestive of the development of a spin at each site in the large $U$ limit. In table (3), we present the exact, true Gutzwiller and VMC bond–orders for two different values of $U$. We see that the VMC and the Gutzwiller bond–orders compare well with the exact values for wide range of correlation strengths. The larger bond order in the Gutzwiller method compared to the exact value is consistent with the observation that this approximation slightly underestimates the role of $U$.

The results presented in tables (2) and (3) are obtained after averaging over equivalent site pairs and up and down spins. The VMC estimates before averaging are not strictly equal for equivalent pairs while the true Gutzwiller numbers reflect the symmetry of the system.

The comparison between MO–VB and exact values in the ground state are favourable for threshold $\approx$ bandwidth, although the MO–VB technique is designed to reproduce excitation gaps for various correlation strengths and is not the method of choice for the ground state properties.
3 Results on Fragments of $C_{60}$

In this section, we present our results on the fragments of $C_{60}$ using the MO–VB technique and compare these with results obtained from the VMC method. We have studied some catacondensed fragments of $C_{60}$ which contain characteristic chemical units of $C_{60}$. These fragments are pyracylene, fluoranthene and corranulene, shown in fig(1). These fragments contain one or more five-membered rings essential for displaying the minimal topological features of $C_{60}$. The trends observed in these systems are expected to be indicative of the behaviour of the full molecule.

3.1 Pyracylene

The pyracylene molecule is a fragment of $C_{60}$ that is amenable to exact calculations. The study of this molecule allows a further test on the approximations besides being of importance in its own right as the molecule is a characteristic fragment of $C_{60}$. In table(4) we present the energy of pyracylene for various values of $U$. The energy obtained from the VMC calculation compares favourably with that from the exact calculation for $U = 1.0$.

In table(5a) we present the bond order data for the unique bonds in pyracylene. From the bond order data, we see that the 1-2 bond or its equivalents is the strongest bond in the system. This trend is found for all correlation strengths studied and is also seen in the exact PPP[24] ground state. The external carbon atoms of the pentagons form almost independent ethylenic
units with a slight extended conjugation as seen from the rather small 2-3 bond order. This is summarized in fig. 2 for $U/t = 1.0$. The bond orders of the internal bonds of the six membered rings are smaller than that of benzene for the same value of $U$ (table(3)) although we can still view the electrons as being delocalized over the benzene rings. This picture is reinforced by the ring currents obtained in the PPP model which show large diamagnetic circulations around the naphthalenic perimeter but paramagnetic circulations around the pentagons. The similarity in PPP and Hubbard bond orders implies similar ring currents in the Hubbard model also. We also expect paramagnetic circulations along the perimeter as found in the PPP model[24].

The kinetic energy contribution to the total ground state energy decreases with increasing $U$ and comparison with the PPP results allows us to estimate that the Hubbard model with an $U_{eff}$ of nearly $3.0t$ should be similar to the PPP model. In table(5b) we present the bond order data of table(5a) normalized with respect to the 1-2 bond. Clearly, the Hubbard model shows smaller bond order variations compared to the PPP model. If the off–site interaction part in the PPP model is treated in the mean field, it would renormalize the transfer part of the Hamiltonian. It is for this reason that the interaction term in the PPP model influences the geometry, while the Hubbard interactions, which are purely on–site have a smaller influence on the geometry of the system.

In tables(6a) and (6b) we present the spin and charge correlations for both on–site and nearest neighbour atom pairs and summarize them in fig. 2 for
The 1-2 bond has a very large antiferromagnetic spin correlation (-0.402) although the sites 1 and 2 have rather large ionic contributions. In the half-filled case, the diagonal (on-site) spin and charge correlation functions in the large $U$ limit are both 1.0, while in the $U \to 0$ limit, they are 0.5 and 1.5 respectively. The large value of $\langle \hat{n}_i^2 \rangle$ and $\langle s_i^z s_j^z \rangle$ for the sites 1 and 2 can be reconciled only if we assume that the spins are aligned antiparallel with a high probability whenever these sites are singly occupied. Thus the ethylenic units show no frustration for delocalization, a trend also evident from the bond order. The spin correlations follow the same trend as the bond orders, with spins at sites 2 and 3 being almost uncorrelated. This implies that the 2–3 bond is not frustrated. The most ionic sites in the molecule are the interior sites, 4 and 11. The exterior benzene sites are least ionic.

The hexagon–hexagon bond is also found to be marginally stronger than the hexagon–pentagon bond, a feature in common with $C_{60}$.

### 3.2 Fluoranthene

The dependance of the energy of fluoranthene on $U$ is given in table(4). Here, exact results are not available for comparison but the energy scales as expected with $U$. From the bond order data of fluoranthene (fig. 3a), we see that the pentagon bonds are weak, while the bonds on the perimeter are strong. The

\[^2\text{These results are obtained by computing } 4\langle s_i^z s_j^z \rangle \text{ and } \langle n_i^2 \rangle, \text{ given that for the half-filled case, in the } U/t = 0 \text{ limit, the probabilities of the Fock space states } (|0\rangle, \ |\uparrow\rangle, \ |\downarrow\rangle \text{and } |\uparrow\downarrow\rangle), \text{ at a given site } i, \text{ are all equal to 0.25. In the large } U \text{ limit, these probabilities are respectively 0, 0.5, 0.5 and 0.}\]
The weakest bond is the bridging 4–5 bond. The bonds forming the benzenic unit and the naphthalenic unit are fairly strong. From the bond order data, we can visualize fluoranthene as weakly bridged benzene and naphthalene units, a feature consistent with an earlier PPP model calculation. Furthermore, the bond order in the isolated hexagon is nearly the same as in benzene. The bonds in the naphthalenic unit show more alternation. We notice that even in fluoranthene, the hexagon–hexagon bond is slightly stronger than the hexagon–pentagon bond. The dependence of bond order on correlation strength is shown in table (7). All the bond orders decrease with increasing $U$. The decrease is sharper at larger $U$ values. The bond orders tend to become uniform within the benzenic and naphthalenic units.

The spin and charge correlations of the nearest neighbour bonds for $U = 1.0$ are shown in fig(3b). The bridging 4–5 bond has a very small antiferromagnetic spin correlation, despite being a nearest neighbour bond. Thus we expect most of the frustration of the pentagon to be manifest in this bond. The charge–charge correlation is largest for this atom pair, and so is the on-site charge correlation. The small spin–spin correlation and the large charge correlations and site ionicities of this bond can be reconciled if we assume that both the sites are simultaneously empty or doubly occupied, and if singly occupied the spins are uncorrelated. It also implies that the most reactive sites in fluoranthene are likely to be these sites. In tables (8a) and (b) we present the dependence of charge and spin correlation on $U$. While all the sites tend to be more covalent, the relative ionicities as well as charge and spin correlations evolve smoothly.
with $U$. We also observe that as $U$ increases, the bond orders decrease, while the spin–spin correlations increase, a trend expected from the Hubbard model.

### 3.3 Corannulene

The energy of the ground state of corannulene for different values of $U$ is presented in table (4). The ground state energy per carbon atom, $\epsilon_c$, is the lowest for this fragment, with $\epsilon_c$ for the fragments obeying the trend corannulene $\approx$ fluoranthene $\approx$ pyracylene. The stabilization decreases with increasing $U$, although the same trend persists. In fig. (4), we present the bond order data of corannulene for $U = 1.0$. Unlike in the other two fragments of $C_{60}$, the pentagonal unit in corannulene is completely enclosed. Therefore the bonds of the pentagon in this fragment most closely approximate the h–p bonds in $C_{60}$. All h–p bonds in corannulene have almost equal bond orders. We observe that the h–p bonds are slightly weaker than the h–h bonds. The outer bonds of corannulene also fall into two categories. The 1–2 like bonds are stronger than the 2–3 like bonds. The higher bond orders of the former group suggest that bonds involving even a single three coordinated carbon atom tend to be weaker due to frustrations encountered during delocalization. The outer bonds with large bond orders evolve into the h–h bonds in $C_{60}$. The bond orders show similar trends for different values of $U$ (table (9)), although the magnitudes decrease with increasing correlation strength.

The spin–spin and charge–charge correlations for $U = 1.0$ are shown in fig. (5). The interior sites are more ionic than the exterior sites. The charge–charge
correlations for atom pairs in the interior sites is larger than for the atom pairs in the exterior sites. The charge–charge correlation for the nearest neighbour pair involving one interior and one exterior atom is in between the values for the purely interior and the purely exterior atom pairs. The smallest charge–charge correlation is found for bonds with the largest bond order. The diagonal spin correlations are nearly uniform at all sites. The spin–spin correlations are nearly the same for any atom pair involving at least one three connected carbon atom, while, for the atom pair with both two-connected carbons, it is much larger. This reflects the bond frustration in bonds involving three connected carbon atoms. These trends continue to hold for larger values of $U$, as seen from tables (10a) and (10b).

4 VMC Ground State Properties of $C_{60}$

We have obtained the ground–state energy of neutral $C_{60}$, with and without bond–alternation for several values of $U$. We have also computed the nearest neighbour bond orders and the charge and spin correlations of $C_{60}$ in both cases. The energies of $C_{60}$ are presented in table (11). These energy values are in good agreement with those of Krivnov et al for the values of $U$ studied[25]. We note that the energy per carbon atom is lower than that of any of the fragments studied. The electronic energy is further reduced on introducing bond alternation. However, we need a reliable estimate of the strain energy[26, 27] to be able to arrive at an equilibrium distortion of the bonds in $C_{60}$. Nev-
ertheless, it is now established that the h–h bonds in \( C_{60} \) are shorter than the h–p bonds\(^{28, 29}\). It is interesting to compare the energy per bond of the fragments with that of \( C_{60} \). The \( U = 1.0 \) values for benzene, pyracylene, fluoranthene, corannulene and \( C_{60} \) are -1.10, -0.95, -0.99, -0.96 and -0.88 respectively. This trend is similar at higher values of \( U \) as well. This brings out clearly that \( C_{60} \) is a more frustrated system than its fragments. The benzene value is clearly outside the range of the fragments of \( C_{60} \).

In table (12) we present bond orders, spin–spin and charge–charge correlations for \( C_{60} \) with and without bond alternation, for the h–h and h–p bonds as well as diagonal charge and spin correlations. We notice that the h–h bond orders are larger than the h–p bond orders for undistorted \( C_{60} \) (uniform bond length) and the difference increases with alternation. While it is possible to optimise the bond length differences for the h–h and the h–p bonds on the basis of Coulson’s empirical formulae, we have not attempted it. From the bond orders for the uniform transfer integral, Coulson’s formula\(^{30, 32}\) predicts a h–h bond length of 1.429 Å and a h–p bond length of 1.453 Å. However, we have chosen the transfer integral of the h–h bond to be 20% stronger than that of the uniform case and the h–p bond to be 10% smaller than in the uniform case. This choice conserves the total transfer integral for the buckyball and allows comparison with the uniform case. The larger alternation has been employed to offset the errors in monte carlo estimates.

The difference in bond order between the h–h and h–p bonds in uniform \( C_{60} \) is larger than that in corannulene. This seems to indicate that the bond
frustrations in $C_{60}$ are more localized on the pentagons than in the fragments of $C_{60}$ or indeed any open frustrated systems. The h–p and h–h charge–charge correlations show the opposite trend when compared to corannulene. This is because the charge–charge correlations are smaller for large bond orders as the transfer of an electron requires the dissimilar occupancy of the sites between which hopping is occurring. The charge–charge correlation for the h–h bond is smaller than for the h–p bond in $C_{60}$. The spin–spin correlation is more antiferromagnetic for the h–h bond than for the h–p bond in $C_{60}$. The h–h bond in $C_{60}$ has weaker antiferromagnetic fluctuations than the h–h bond in corannulene, while the h–p bond in $C_{60}$ has smaller antiferromagnetic fluctuations than the h–p bond in corannulene. This trend holds for all values of $U$.

The site ionicities of the carbon sites in $C_{60}$ are smaller than the interior sites in corannulene, as can be seen from the smaller diagonal charge correlation in the former. This is also confirmed by the larger diagonal spin correlation in $C_{60}$ compared with that for the pentagonal sites in corannulene.

The spin and charge correlations for the h–h bond increase when alternation in the transfer integral is introduced, while these quantities decrease for the h–p bond. The site ionicities are smaller than those of uniform $C_{60}$. This trend persists for all values of $U$ studied by us.

The average bond order of a molecule gives the extent of kinetic stabilization due to delocalization. It is interesting to compare the average bond orders for $U/t = 0$ for benzene, $C_{60}$ and graphite[?], which are $2/3$, 0.518 and 0.525.
In benzene and $C_{60}$ the bond orders are marginally reduced for $U/t = 1.0$ to 0.66 and 0.513 respectively. A similar trend is expected in graphite, upon introducing correlations. Thus, it appears that in $C_{60}$ the kinetic stabilization is only slightly smaller than in graphite, in spite of bond frustration in the former due to the five-membered rings. This result could be an artefact of the Hubbard model; for even in the mean-field limit, extended range interactions renormalize the transfer integrals, leading to contributions to the kinetic energy and hence to the bond orders. It is also interesting to compare the pentagons in $C_{60}$ with the cyclopentadienyl radical. The pentagonal bond order in this molecule is 0.58 while the h–p bond order in $C_{60}$ is 0.47 for $U = 1.0$. Thus the pentagons in $C_{60}$ are more frustrated than a single pentagonal unit.

The value of the Gutzwiller parameter $g$ for which the energy is a minimum indicates the overall extent of suppression of the doubly occupied sites in a given system. In table (13), the value of the Gutzwiller parameter $g$ for which the energy is a minimum is given for all the systems reported in this paper. There is no systematic variation in $g$ across the fragments and all the systems seem to suppress double occupancies to a similar extent for a given value of $U$.

5 Summary

We have studied the fragments of $C_{60}$ by various CI techniques as well as the VMC. Comparison of these studies allows us to derive reasonable monte carlo parameters for the simulation of larger systems like $C_{60}$. The bond
order analysis of these molecules allows us to visualise structures which are consistent with the spin and charge correlations. We are able to observe the evolution of the properties of the fragments towards the properties of \( C_{60} \) through the properties of the hexagon–hexagon like and hexagon–pentagon like bonds. Corannulene is found to be the fragment of \( C_{60} \) that approximates the full molecule most closely. We have studied the uniform and bond alternated models for \( C_{60} \). Even when the transfer integral is uniform, the bond orders of \( C_{60} \) show more marked alternation than the fragments.

Even though the VMC is an approximation over and above that inherent in the Gutzwiller wavefunction it is interesting to see that the VMC technique provides a reasonable description of the ground state electronic structure of molecular systems. The VMC energies are in good agreement with model exact energies for intermediate values of \( U/t \), but progressively deteriorates for large \( U/t \). We are currently involved in extending the Gutzwiller type of VMC approach to models with nearest neighbour Coulomb interactions.

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Table 1. Ground state energy of benzene (in units of $t$) as a function of $U$ from exact and approximate calculations. The $g_{\text{min}}$ values are given in parantheses. The VMC energies do not change on doubling the number of MPE for sampling.

| $U$ | $E_{\text{exact}}$ | $E_{\text{MO-VB}}$ | $E_{\text{Gutz}}$ | $E_{\text{VMC}}$ |
|-----|---------------------|---------------------|-------------------|------------------|
| 0.5 | -7.2744             | -7.2742             | -7.2741 (0.91)    | -7.274 (0.91)    |
| 1.0 | -6.6012             | -6.5963             | -6.5964 (0.83)    | -6.597 (0.83)    |
| 2.0 | -5.4105             | -5.3744             | -5.3868 (0.69)    | -5.388 (0.71)    |
| 4.0 | -3.6697             | -3.3516             | -3.5371 (0.47)    | -3.538 (0.46)    |

Table 2. Spin–Spin correlations ($4 < s_i^z s_j^z >$) and charge–charge correlations ($< n_i n_j >$) of benzene for $U = 1.0$ and 4.0, from exact and approximate calculations. The VMC values do not change on doubling the Monte Carlo sampling size.

| $U$ | $i,j$ | $4 < s_i^z s_j^z >$ | $< n_i n_j >$ |
|-----|-------|---------------------|----------------|
|     | Exact | Gutz | VMC | Exact | Gutz | VMC |
| 1.0 | 1,1   | 0.567 | 0.565 | 0.557 | 1.432 | 1.435 | 1.443 |
| 1.0 | 1,2   | -0.267 | -0.265 | -0.245 | 0.816 | 0.817 | 0.812 |
| 1.0 | 1,3   | 0.022 | 0.016 | 0.011 | 0.989 | 0.989 | 0.976 |
| 1.0 | 1,4   | -0.077 | -0.068 | -0.062 | 0.960 | 0.953 | 0.952 |
| 4.0 | 1,1   | 0.778 | 0.751 | 0.750 | 1.222 | 1.249 | 1.250 |
| 4.0 | 1,2   | -0.435 | -0.404 | -0.395 | 0.905 | 0.911 | 0.911 |
| 4.0 | 1,3   | 0.140 | 0.095 | 0.077 | 0.999 | 0.979 | 0.979 |
| 4.0 | 1,4   | -0.188 | -0.131 | -0.113 | 0.989 | 0.971 | 0.971 |
Table 3. Bond–orders of the nearest neighbour bond in benzene for $U = 1.0$ and 4.0 from exact and approximate calculations. The VMC values do not change on doubling the Monte Carlo sampling size.

| $U$ | Exact  | Gutz   | VMC  |
|-----|--------|--------|------|
| 0.5 | 0.6646 | 0.6646 | 0.664|
| 1.0 | 0.6582 | 0.6584 | 0.660|
| 2.0 | 0.6316 | 0.6344 | 0.636|
| 4.0 | 0.5278 | 0.5441 | 0.545|

Table 4. Ground state energies of pyracylene, fluoranthene and corannulene (in units of $t$) from restricted CI and VMC calculations. Numbers in parantheses are the energies per site. MO–VB energies are not given for larger values of $U$ as the technique is known to give poor ground state energies for large $U$. The VMC values do not change on doubling the Monte Carlo sampling size.

| $U$ | Pyracylene | Fluoranthene | Corannulene |
|-----|------------|--------------|-------------|
|     | $E_{MO-VB}$ | $E_{VMC}$    | $E_{MO-VB}$ | $E_{VMC}$    | $E_{MO-VB}$ | $E_{VMC}$    |
| 0.5 | -17.7002   | -17.713(-1.27)| -20.5231    | -20.558(-1.28)| -26.2689    | -26.306(-1.32)|
| 1.0 | -16.0631*  | -16.116(-1.15)| -18.5943    | -18.730(-1.17)| -23.8655    | -24.007(-1.20)|
| 2.0 | -12.9817   | -13.235(-0.95)| -14.8631    | -15.422(-0.96)| -19.2221    | -19.847(-0.99)|
| 4.0 | —         | -8.666 (-0.62)| —           | -10.164 (-0.64)| —           | -13.158(-0.66)|

* exact energy obtained from full CI calculation in the singlet subspace of dimension 2760615 is -16.13
Table 5a. Bond-orders of the unique bonds and total kinetic energy (KE) in the ground state of pyracylene from VMC calculations. The VMC values do not change on doubling the Monte Carlo sampling size.

| $i,j$ | $U = 0.5$ | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ | PPP(exact) |
|-------|-----------|-----------|-----------|-----------|------------|
| 1,2   | 0.819     | 0.819     | 0.795     | 0.695     | 0.816      |
| 2,3   | 0.399     | 0.402     | 0.382     | 0.330     | 0.239      |
| 3,4   | 0.517     | 0.509     | 0.494     | 0.442     | 0.455      |
| 5,6   | 0.652     | 0.647     | 0.630     | 0.562     | 0.697      |
| 6,9   | 0.609     | 0.605     | 0.581     | 0.518     | 0.604      |
| 4,11  | 0.531     | 0.531     | 0.519     | 0.463     | 0.526      |
| KE    | -19.365   | -19.228   | -18.594   | -16.448   | -17.860    |
Table 5b. Normalized bond orders of the unique bonds in the ground state of pyracylene from VMC calculations.

| $i,j$ | $U = 0.5$ | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ | PPP(exact) |
|-------|-----------|-----------|-----------|-----------|------------|
| 1,2   | 1.000     | 1.000     | 1.000     | 1.000     | 1.000      |
| 2,3   | 0.490     | 0.491     | 0.480     | 0.474     | 0.293      |
| 3,4   | 0.631     | 0.621     | 0.621     | 0.636     | 0.558      |
| 5,6   | 0.795     | 0.790     | 0.793     | 0.809     | 0.854      |
| 6,9   | 0.790     | 0.739     | 0.731     | 0.745     | 0.740      |
| 4,11  | 0.648     | 0.648     | 0.652     | 0.665     | 0.645      |
Table 6a. On–site and nearest neighbour VMC spin–spin correlations $(4 < s_i^z s_j^z >)$ of pyracylene for different $U/t$ values. The VMC values do not change on doubling the Monte Carlo sampling size. Numbers in parentheses are the exact AO-VB results, given for comparison.

| $i, j$ | Nearest neighbour | On–site | | | | |
|---|---|---|---|---|---|---|
|   | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ |
| 1,2 | -0.402 (-0.4308) | -0.475 | -0.595 | 1,1 | 0.565 (0.5849) | 0.625 | 0.744 |
| 2,3 | -0.099 (-0.0930) | -0.107 | -0.138 | 3,3 | 0.551 (0.5563) | 0.616 | 0.711 |
| 3,4 | -0.155 (-0.1532) | -0.182 | -0.241 | 4,4 | 0.549 (0.5477) | 0.604 | 0.706 |
| 5,6 | -0.250 (-0.2598) | -0.254 | -0.382 | 6,6 | 0.554 (0.5651) | 0.617 | 0.719 |
| 4,11 | -0.164 (-0.1703) | -0.205 | -0.273 |             |             |             |
| 6,9 | -0.225 (-0.2219) | -0.260 | -0.326 |             |             |             |
Table 6b. On–site and nearest neighbour VMC charge–charge correlations ($<n_in_j>$) of pyracylene for different $U/t$ values. The VMC values do not change on doubling the Monte Carlo sampling size.

| $i,j$ | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ | $i,j$ | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ |
|-------|-----------|-----------|-----------|-------|-----------|-----------|-----------|
| 1,2   | 0.794     | 0.841     | 0.929     | 1,1   | 1.514     | 1.444     | 1.321     |
| 2,3   | 0.964     | 0.972     | 0.992     | 3,3   | 1.431     | 1.374     | 1.281     |
| 3,4   | 0.964     | 0.984     | 1.012     | 4,4   | 1.621     | 1.570     | 1.400     |
| 5,6   | 0.737     | 0.776     | 0.846     | 6,6   | 1.228     | 1.240     | 1.171     |
| 6,9   | 0.702     | 0.738     | 0.810     |       |           |           |           |
| 4,11  | 1.059     | 1.064     | 1.393     |       |           |           |           |
Table 7. Bond-orders of the unique bonds and total kinetic energy (KE) in the ground state of fluoranthene from VMC calculations. The VMC values do not change on doubling the Monte Carlo sampling size.

| $i,j$ | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ |
|-------|-----------|-----------|-----------|
| 1,2   | 0.643     | 0.612     | 0.518     |
| 2,3   | 0.666     | 0.637     | 0.550     |
| 3,4   | 0.611     | 0.591     | 0.519     |
| 4,5   | 0.388     | 0.377     | 0.320     |
| 5,6   | 0.657     | 0.630     | 0.548     |
| 6,7   | 0.611     | 0.593     | 0.514     |
| 7,8   | 0.707     | 0.676     | 0.579     |
| 8,9   | 0.546     | 0.522     | 0.451     |
| 4,14  | 0.566     | 0.539     | 0.472     |
| 5,16  | 0.512     | 0.494     | 0.436     |
| 9,16  | 0.526     | 0.512     | 0.446     |
| KE    | -22.256   | -21.397   | -18.539   |
Table 8a. On–site and nearest neighbour VMC spin–spin correlations $(4 < s_i^z s_j^z >)$ of fluoranthene for different $U/t$ values. The VMC values do not change on doubling the Monte Carlo sampling size.

| Nearest neighbour | On–site | Nearest neighbour | On–site |
|------------------|---------|------------------|---------|
| $i, j$           | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ | $i, j$           | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ |
| 1,2              | -0.259  | -0.300  | -0.395  | 1,1              | 0.5617  | 0.6358  | 0.7548  |
| 2,3              | -0.284  | -0.327  | -0.409  | 3,3              | 0.5702  | 0.6372  | 0.7399  |
| 3,4              | -0.228  | -0.283  | -0.362  | 4,4              | 0.552   | 0.619   | 0.729   |
| 4,5              | -0.087  | -0.109  | -0.137  | 5,5              | 0.561   | 0.622   | 0.729   |
| 5,6              | -0.260  | -0.305  | -0.403  | 6,6              | 0.552   | 0.621   | 0.738   |
| 6,7              | -0.222  | -0.271  | -0.360  | 7,7              | 0.565   | 0.630   | 0.745   |
| 7,8              | -0.303  | -0.361  | -0.452  | 8,8              | 0.557   | 0.626   | 0.744   |
| 8,9              | -0.176  | -0.206  | -0.280  | 9,9              | 0.551   | 0.620   | 0.731   |
| 4,14             | -0.187  | -0.220  | -0.298  | 16,16            | 0.561   | 0.624   | 0.722   |
| 5,16             | -0.167  | -0.211  | -0.271  |                    |         |         |         |
| 9,16             | -0.166  | -0.176  | -0.233  |                    |         |         |         |
Table 8b. On–site and nearest neighbour VMC charge–charge correlations \( (<n_i n_j>) \) of fluoranthene for different \( U/t \) values.

| \( i, j \) | Nearest neighbour | \( U = 1.0 \) | \( U = 2.0 \) | \( U = 4.0 \) | On–site | \( U = 1.0 \) | \( U = 2.0 \) | \( U = 4.0 \) |
|--------|------------------|-------------|-------------|-------------|---------|-------------|-------------|-------------|
| 1,2    | 0.835            | 0.874       | 0.926       | 1,1         | 1.452   | 1.373       | 1.249       |
| 2,3    | 0.807            | 0.859       | 0.911       | 3,3         | 1.397   | 1.364       | 1.260       |
| 3,4    | 0.864            | 0.898       | 0.945       | 4,4         | 1.523   | 1.433       | 1.318       |
| 4,5    | 1.013            | 1.003       | 1.016       | 5,5         | 1.515   | 1.443       | 1.321       |
| 5,6    | 0.800            | 0.841       | 0.909       | 6,6         | 1.344   | 1.291       | 1.209       |
| 6,7    | 0.790            | 0.825       | 0.883       | 7,7         | 1.435   | 1.373       | 1.234       |
| 7,8    | 0.839            | 0.849       | 0.861       | 8,8         | 1.379   | 1.294       | 1.193       |
| 8,9    | 0.839            | 0.860       | 0.914       | 9,9         | 1.452   | 1.384       | 1.278       |
| 4,14   | 0.934            | 0.939       | 0.981       | 16,16       | 1.508   | 1.452       | 1.343       |
| 5,16   | 0.965            | 0.986       | 0.998       |             |         |             |             |
| 9,16   | 0.920            | 0.949       | 0.981       |             |         |             |             |
Table 9. Bond-orders of the unique bonds and total kinetic energy (KE) in the ground state of corannulene from VMC calculations.

| i, j | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ |
|------|-----------|-----------|-----------|
| 1,2  | 0.745     | 0.721     | 0.641     |
| 2,3  | 0.529     | 0.509     | 0.454     |
| 16,17| 0.504     | 0.489     | 0.433     |
| 3,17 | 0.551     | 0.535     | 0.491     |
| KE   | -28.562   | -27.673   | -24.751   |

Table 10a. On–site and nearest neighbour VMC spin–spin correlation $< s_i^z s_j^z >$ of corannulene for different $U/t$ values.

| Nearest neighbour | On–site |
|------------------|---------|
|                  | $i, j$  | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ | $i, j$  | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ |
|                  |         | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ |         | $U = 1.0$ | $U = 2.0$ | $U = 4.0$ |
| 1,2              | 1,1     | 0.552     | 0.612     | 0.720     |
| 2,3              | 3,3     | 0.539     | 0.604     | 0.702     |
| 16,17            | 16,16   | 0.537     | 0.601     | 0.699     |
| 3,17             | 3,17    | 0.551     | 0.535     | 0.491     |

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Table 10b. On–site and nearest neighbour VMC charge–charge correlations \(< n_i n_j >\) of corannulene for different \(U/t\) values.

| Nearest neighbour | On–site |
|-------------------|---------|
| \(i, j\) \(U = 1.0\) | \(U = 2.0\) | \(U = 4.0\) | \(i, j\) \(U = 1.0\) | \(U = 2.0\) | \(U = 4.0\) |
| 1,2                | 0.725   | 0.777   | 0.847   | 1,1                | 1.414   | 1.359   | 1.251   |
| 2,3                | 0.840   | 0.870   | 0.915   | 3,3                | 1.422   | 1.357   | 1.284   |
| 16,17              | 0.997   | 1.001   | 1.017   | 16,16              | 1.567   | 1.494   | 1.378   |
| 3,17               | 0.895   | 0.917   | 0.957   |                     |         |         |         |

Table 11. Ground state energy of uniform and bond alternant \(C_{60}\) for various values of \(U\) from VMC.

| \(U\) | uniform | bond alternant |
|-------|---------|----------------|
|       | E       | E/site E/bond | E       | E/site E/bond     |
| 1.0   | -78.891 | -1.315 -0.877 | -81.448 | -1.358 -0.905     |
| 2.0   | -66.074 | -1.101 -0.734 | -68.733 | -1.146 -0.764     |
| 3.0   | -55.669 | -0.928 -0.619 | -57.473 | -0.958 -0.639     |
| 4.0   | -44.678 | -0.745 -0.496 | -47.768 | -0.796 -0.531     |
| 5.0   | -36.088 | -0.602 -0.401 | -39.566 | -0.695 -0.440     |
| 6.0   | -28.787 | -0.480 -0.320 | -32.435 | -0.541 -0.360     |
Table 12. On–site and nearest neighbour VMC charge–charge correlations \((< n_i n_j >)\) and spin–spin correlations \((4 < s^z_i s^z_j >)\) and bond orders of uniform and bond alternant \(C_{60}\) for different \(U/t\) values.

|   | uniform | bond alternant |
|---|---------|----------------|
|   | h–h     | h–p diag       | h–h     | h–p         |
| 1.0 | bo 0.597 0.471 — | 0.849 0.367 — |
|   | s-s -0.212 -0.132 0.550 | -0.296 -0.099 0.5500 |
|   | c-c 0.847 0.904 1.450 | 0.784 0.927 1.450 |
| 2.0 | bo 0.582 0.461 — | 0.827 0.359 — |
|   | s-s -0.241 -0.152 0.589 | -0.336 -0.115 0.601 |
|   | c-c 0.872 0.919 1.402 | 0.819 0.938 1.399 |
| 3.0 | bo 0.535 0.414 — | 0.756 0.321 — |
|   | s-s -0.314 -0.191 0.690 | -0.431 -0.143 0.699 |
|   | c-c 0.912 0.947 1.310 | 0.879 0.960 1.301 |
| 4.0 | bo 0.448 0.336 — | 0.634 0.254 — |
|   | s-s -0.404 -0.233 0.787 | -0.545 -0.169 0.799 |
|   | c-c 0.949 0.970 1.258 | 0.928 0.977 1.201 |
Table 13. Minimum value of the Gutzwiller parameter $g$ for fragments of $C_{60}$, uniform and bond alternant $C_{60}$ (A and B).

| $U$ | pyracylene | fluoranthene | corannulene | $C_{60}$(A) | $C_{60}$(B) |
|-----|------------|--------------|-------------|-------------|-------------|
| 0.5 | 0.91       | 0.92         | 0.93        | —           | —           |
| 1.0 | 0.85       | 0.83         | 0.88        | 0.85        | 0.87        |
| 2.0 | 0.69       | 0.69         | 0.71        | 0.73        | 0.74        |
| 4.0 | 0.50       | 0.47         | 0.51        | 0.53        | 0.53        |
References

[1] Kroto, H. W.; Heath, J. R.; O’Brien, S. C.; Curl, R. F.; Smalley, R. E. Nature 1985, 318, 162.

[2] Kratschmer, W.; Lamb, L. D.; Fostiropoulos, L. K.; Huffman, D. R. Nature 1990, 347, 354.

[3] Fleming, R. M.; Ramírez, A. P.; Rosseinsky, M. J.; Murphy, D. W.; Had- don, R. C.; Zahurak, S. M.; Makhija, A. V. Nature 1991, 352, 787.

[4] Allemand, P. M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Gruner, G.; Thompson, J. E. Science 1991, 253, 301.

[5] Stephens, P. W.; Cox, D.; Lauher, J. W.; Mihaly, L.; Wiley, J. B.; Alle- mand, P. M.; Hisch, A.; Holczer, K.; Li, Q.; Thompson, J. D.; Wudl, F. Nature 1992, 355, 331.

[6] Ramasesha, S.; Soos, Z. G.; J. Chem. Phys. 1984, 80, 3278.

[7] Srinivasan, B.; Ramasesha, S.; Full. Sci. and Tech., in press.

[8] Ramasesha, S.; Galvao, D. S.; Soos, Z. G. J. Phys. Chem. 1993, 97, 2824.

[9] Chakravarthy, S.; Gelfand, M. P.; Kivelson, S. Science 1991, 254, 970.

[10] Gutzwiller, M. C. Phys. Rev. Lett. 1963, 10, 159; Phys. Rev.1964, 134, A993; ibid. 1965, 137, A1726.
[11] Joyes, P.; Tarento, R. J. *Phys. Rev.* **1992**, *B45*, 12077.

[12] Hubbard, J. *Proc. Roy. Soc. Lond.* **1964**, *A276*, 238; *ibid.* **1964**, *A277*, 237; *ibid.* **1964**, *A281*, 401.

[13] Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*, Macmillan: London, 1982.

[14] Srinivasan, B.; Ramasesha, S. *Solid State Commun.* **1992**, *81*, 831; Ramasesha, S.; Srinivasan, B. *Ind. J. of Chem.* **1992**, *31A,B*, F56.

[15] Soos, Z. G.; Ramasesha, S. *Valence bond theory and Chemical structure*, ed. D. J. Klein and N. Trinajstic; Elsevier: Amsterdam, 1990; p81.

[16] Lowdin, P. -O. *J. Chem. Phys.* **1950**, *18*, 365.

[17] Ramasesha, S. *J. Mol. Struct.* **1989**, *194*, 149.

[18] Soos, Z. G.; Ramasesha, S. *Phys. Rev.* **1984**, *B29*, 5410.

[19] Bijl, A. *Physica* **1940**, *7*, 860.

[20] Jastrow, R. *Phys. Rev.* **1955**, *98*, 1479.

[21] Yokoyama, H.; Shiba, H. *J. Phys. Soc. Jpn.* **1987**, *56*, 1490.

[22] Ceperley, D. M.; Chester, G. V.; Kalos, K. H. *Phys. Rev.* **1977**, *B16*, 3081.
[23] Press, W. H.; Teukolsky, S. A.; Vellering, W. T.; Flannery, B. P. *Numerical Recipes* 2nd ed.; Cambridge University Press: Cambridge, 1992.

[24] Chakrabarti, A.; Anusooya, Y.; Ramasesha, S. *J. Mol. Struct.*, in press.

[25] Krivnov, V. Ya.; Shamovsky, I. L.; Tornau, E. E.; Rosengren, A. *Phys. Rev.* **1994**, *B50*, 12144.

[26] Varma, C. M.; Zaanen, J.; Raghavachari, K.; *Science* **1991**, *254*, 989.

[27] Schulter, M.; Lannoo, M.; Needels, M.; Baraff, G. A.; Tomanek, D. *Phys. Rev. Lett.* **1992**, *68*, 526.

[28] David, W. I. F.; Ibberson, R. M.; Matthewman, J. C.; Prassides, K.; Denis, T. J. S.; Hare, J. P.; Kroto, W. H.; Taylor, R.; Walton, D. R. M. *Nature* **1991**, *353*, 147.

[29] Hedberg, K.; Hedberg, L.; Bethune, D. S.; Brown, C. A.; Dorn, H. C.; Johnson, R. D.; de Vries, M. *Science* **1991**, *254*, 410.

[30] Coulson, C. A. *Proc. Royal Soc.* **1939**, *A169*, 413.

[31] Coulson, C. A.; Mallion, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 592.

[32] Coulson, C. A.; Mallion, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 592.
Figure Captions

**Figure 1.** Structures of Pyracylene, Fluoranthene and Corannulene.

**Figure 2.** Bond orders(A), diagonal charge–charge (spin–spin) correlations(B), nearest neighbour charge–charge correlations(C) and nearest neighbour spin–spin correlations(D) for unique sites and bonds of pyracylene for $U = 1.0$.

**Figure 3a.** Bond orders and diagonal charge–charge (spin–spin) correlations for unique bonds and sites in fluoranthene for $U = 1.0$. The axes of symmetry are shown.

**Figure 3b.** Unique nearest neighbour charge–charge correlations and spin–spin correlations of fluoranthene for $U = 1.0$.

**Figure 4.** Bond orders and diagonal charge–charge (spin–spin) correlations of corannulene for $U = 1.0$. The difference between symmetry related quantities indicates the extent of scatter in VMC estimates.

**Figure 5.** Nearest neighbour charge–charge correlations and spin–spin correlations in corannulene for $U = 1.0$. The difference between symmetry related quantities indicates the extent of scatter in VMC estimates.