Competition between structural distortion and magnetic moment formation in fullerene C\textsubscript{20}

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(Dated: May 18, 2009)

Abstract

We investigated the effect of on-site Coulomb interactions on the structural and magnetic ground state of the fullerene C\textsubscript{20} based on density-functional-theory calculations within the local density approximation plus on-site Coulomb corrections (LDA+U). The total energies of the high symmetry (I\textsubscript{h}) and distorted (D\textsubscript{3d}) structures of C\textsubscript{20} were calculated for different spin configurations. The ground state configurations were found to depend on the forms of exchange-correlation potentials and the on-site Coulomb interaction parameter U, reflecting the subtle nature of the competition between Jahn-Teller distortion and magnetic instability in fullerene C\textsubscript{20}. While the non-magnetic state of the distorted D\textsubscript{3d} structure is robust for small U, a magnetic ground state of the undistorted I\textsubscript{h} structure emerges for U larger than 4 eV when the LDA exchange-correlation potential is employed.

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I. INTRODUCTION

Since the discovery of fullerene C\textsubscript{60} \cite{1} various research activities on alternative fullerene structures of carbon materials have flourished due to their noble physical properties and potential applications as next generation electronic devices. The smallest fullerene C\textsubscript{20} has been actively studied after its first successful production by Prinzbach et al. \cite{2}. Although there have been many theoretical predictions on its intriguing properties such as superconductivity, \cite{3} vibrational modes, \cite{4, 5} and transport \cite{6, 7, 8} along the line of fullerene-based molecular electronics, \cite{9, 10} C\textsubscript{20} has been a challenge for theorists since long before its experimental synthesis. For instance, the stable structural configuration of C\textsubscript{20} has not been clearly understood. The effort to determine the stable structure and relative stability of C\textsubscript{20} isomers, e.g., ring, bowl, and cage, has raised a question on the contribution of electron correlation energy to the structural stability \cite{11, 12, 13, 14}. One of the difficulties in predicting the most stable C\textsubscript{20} isomer lies in the treatment of the exchange-correlation (XC) energy. It was shown that density-functional-theory (DFT) calculations gave qualitatively different results depending on the XC functional such as local density approximation (LDA), generalized gradient approximation (GGA), and Hartree-Fock (HF). Even the quantum Monte Carlo (QMC) results were different from LDA, GGA, HF and hybrid DFT\cite{13}.

The prediction of the ground state atomic structure of fullerene C\textsubscript{20} has suffered the similar problem. The high symmetry I\textsubscript{h} structure of the C\textsubscript{20} cage is known to be unstable with respect to the Jahn-Teller (JT) distortion. According to Galli et al. \cite{14}, both LDA and GGA predicted D\textsubscript{3d} as the symmetry of the most stable Jahn-Teller distorted cage structure, which is consistent with the tight-binding molecular-dynamics (TBMD) result by Yamamoto et al. \cite{8}. However, the hybrid DFT calculation by Saito and Miyamoto \cite{4} determined C\textsubscript{2h} to be the most stable one, while C\textsubscript{2} or D\textsubscript{5d} were chosen by the HF calculations\cite{14}. Sometimes even the same kind of calculations made by different groups have given different predictions (see, for example, Ref. \cite{14}). As Grossman et al. pointed out, this small molecular carbon system, C\textsubscript{20}, demonstrates the importance of the highly accurate treatment of electron correlations \cite{13}.

Recently Lin et al. \cite{15, 16} took a different perspective to this issue. By considering the fullerene C\textsubscript{20} as a superatom with 20 valence electrons, they set up a tight binding model taking account of the strong hybridization of p\textsubscript{\pi} orbitals with p\textsubscript{\sigma}, which arises from the extreme curvature of the C\textsubscript{20} cage. Expecting the important role of the on-site Coulomb interaction, they carried out QMC and exact diagonalization (ED) calculations for the Hubbard model hamiltonian...
for $C_{20}$. As a result, it was found that $C_{20}$ with both $I_h$ and $D_{3d}$ structures undergoes a magnetic-to-non-magnetic and non-magnetic-to-magnetic transitions for $I_h$ and $D_{3d}$, respectively, as $U/t$ increases\cite{15,16}.

To investigate the effect of the on-site Coulomb interaction in connection with its ground state atomic and magnetic structures, we performed LDA+$U$ and GGA+$U$ calculations\cite{17} and calculated optimized structure under the symmetry constraint of $I_h$ and $D_{3d}$. Our result showed that the non-magnetic $D_{3d}$ structure is more stable than magnetic $I_h$ for small values of $U$ less than 4 eV regardless of the choice of the XC functionals, which is consistent with previous works\cite{8,14}. However, when $U > 4$ eV, the LDA+$U$ calculations predict a magnetic state with $\mu = 2\mu_B$ to be a ground state, which is different from GGA+$U$. This result indicates that there are subtleties in the competition between the Jahn-Teller structural instability and the magnetic instability enhanced by Coulomb correlations. Further the dependence on the exchange-correlation functionals suggests the importance of electron correlation effects in determination of the $C_{20}$ ground state.

II. COMPUTATIONAL METHODS

A. LDA+$U$ Method

In order to describe on-site Coulomb interactions for the carbon $2p$ orbitals, which are relatively localized in a small-sized cluster like $C_{20}$, we employed the LDA+$U$ (GGA+$U$) method\cite{17,18}. In our LDA+$U$ (GGA+$U$) approach, the total energy functional is written as\cite{18}

$$E_{\text{LDA}+U(GGA)} = E_{\text{LDA}(GGA)} + E_U^0 - E_{\text{dc}}^U,$$

where $E_{\text{LDA}(GGA)}$ is the LDA (GGA) energy functional and $E_U^0$ is given by a spherically averaged screened-Coulomb energy $U$ and an exchange energy $J$:

$$E_U^0 = \frac{1}{2} \sum_\alpha U_\alpha \sum_{\sigma m \sigma'} n_{\sigma m}^\sigma n_{\sigma m'}^{-\sigma} + \frac{1}{2} \sum_\alpha (U_\alpha - J_\alpha) \sum_{\sigma, m \neq m'} n_{\sigma m}^\sigma n_{\sigma m'}^{-\sigma},$$

where $\sigma$ is the spin index, $\alpha \equiv (ilp)$ with the site index $i$, the angular momentum quantum number $l$, and the multiplicity number of the radial basis function $p$. $n_{\sigma m}^\sigma$ is an eigenvalue of the occupation number matrix. Here the $U$- and the $J$-values are assumed to depend only on the index $\alpha$, but to be independent of the azimuthal quantum number $m$, which is regarded as a simplification of the Hartree-Fock theory by using a spherical average. The double-counting term $E_{dc}^U$ can be written
as

\[ E_{dc}^U = \frac{1}{2} \sum_\alpha U_\alpha N_\alpha (N_\alpha - 1) - \frac{1}{2} \sum_\alpha J_\alpha \sum_\sigma N_{\sigma \alpha}^\sigma (N_{\sigma \alpha}^\sigma - 1), \]  

(3)

where \( N_{\sigma \alpha}^\sigma = \sum_m n_{\alpha m}^\sigma \) and \( N_\alpha = N_\alpha^\uparrow + N_\alpha^\downarrow \). Therefore, \( E_U \equiv E_U^0 - E_{dc}^U \) reads

\[ E_U = \frac{1}{2} \sum_\alpha (U_\alpha - J_\alpha) \sum_\sigma \{ \text{Tr}(n_\alpha^\sigma) - \text{Tr}(n_{\sigma \alpha}^\sigma n_{\alpha}^\sigma) \}, \]

(4)

and it is the term that describes the on-site Coulomb interactions. The effective \( U \)-value, defined by \( U = U_\alpha - J_\alpha \), can be treated as a numerical parameter, and it is clear from Eq. (4) that LDA+\( U \) (GGA+\( U \)) method is equivalent to LDA (GGA) in \( U \to 0 \) limit. We used the previously proposed ‘dual’ representation \[^{18}\] which is proven to be successful for various materials \[^{19, 20, 21}\].

We considered the on-site Coulomb interaction \( U \) for the carbon \( 2p \) orbitals, which are relatively localized in a small-sized cluster like \( C_{20} \). In our LDA+\( U \) and GGA+\( U \) calculations, we used the previously proposed ‘dual’ representation \[^{18}\], which is proven to be successful for various materials \[^{19, 20, 21}\].

\section*{B. Computation Details}

We performed cluster calculations based on the DFT by employing a linear-combination-of-localized-pseudo-atomic orbitals (LCPAO) as a basis set. Ceperley-Alder \[^{22, 23}\] and Perdew-Burke-Ernzerh \[^{24}\] type exchange-correlation energy functional were adopted for LDA and GGA calculation, respectively. We used double valence orbitals as a basis set which were generated by a confinement potential scheme with the cutoff radius of 5.0 a.u.. Troullier-Martins type pseudopotentials with a partial core correction were used to replace the deep core potentials by norm-conserving soft potentials in a factorized separable form with multiple projectors. The real space grid techniques were used with the energy cutoff of 160 Ry in numerical integrations and the solution of the Poisson equation using fast Fourier transformations (FFT). In addition, the projector expansion method was employed to accurately calculate three-center integrals associated with the deep neutral atom potential with \( L_{\text{max}} = 6 \) and \( N_{\text{rad}} = 4 \). All the DFT calculations were performed using our DFT OpenMX code\[^{25}\].
III. RESULT AND DISCUSSION

Figure 1 shows a schematic diagram of the Hückel’s molecular orbital levels around the Fermi energy for the magnetic \( I_h \) and the Jahn-Teller (JT) distorted \( D_{3d} \) structure of fullerene C\(_{20}\). In the highly symmetric \( I_h \) structure, the highest-occupied-molecular-orbital (HOMO) states are four-fold degenerate and partially filled by two valence electrons. Due to the electronic degeneracy, the \( I_h \) structure C\(_{20}\) is Jahn-Teller active and can undergo a structural distortion. Consequently the Jahn-Teller distorted \( D_{3d} \) structure leads to a finite gap in between the HOMO level and the lowest-unoccupied-molecular-orbital (LUMO) states. Since the HOMO state is occupied by a singlet pair, the \( D_{3d} \) ground state becomes non-magnetic. On the other hand, the \( I_h \) C\(_{20}\) ground state can be magnetic due to a kind of the Hund’s rule coupling present in this ‘superatom’, where the magnetic exchange energy between the HOMO electrons favors the magnetically aligned spin state of the undistorted \( I_h \) structure.

The calculated density-of-states (DOS) in Fig. 2 clearly shows the different electronic structure of these two structures. The dotted blue and solid red lines correspond to the \( U = 0 \) and \( U = 2 \) eV calculation, respectively. The Fermi level of \( I_h \) C\(_{20}\) is located at the middle of a majority spin peak (Fig. 2(a)), whereas \( D_{3d} \) has a finite HOMO-LUMO gap (Fig. 2(b)), which is consistent with the Hückel’s molecular orbital pictures in Fig. 1. While the electronic states of the JT-distorted \( D_{3d} \) structure are hardly affected by the change of on-site \( U \) values from 0 to 2 eV, the exchange split of the undistorted \( I_h \) structure is significantly enhanced even for the moderate on-site interaction of \( U = 2 \) eV. Considering the enhanced exchange interactions, we tried to explore a possible contribution of the on-site Coulomb interactions to the stabilization of the magnetic \( I_h \) structure over that of the JT structural distortion.

Figure 3 shows the calculated total energies by LDA+\( U \) (Fig. 3(a)) and GGA+\( U \) (Fig. 3(b)) as a function of \( U \). For comparison, we also calculated the total energies of the non-magnetic (NM) phase of \( I_h \). The total energies of FM-\( I_h \), NM-\( I_h \), and NM-\( D_{3d} \) are represented by the dotted grey, dotted blue, and solid red lines, respectively. The total energy of FM-\( I_h \) is set at zero as a reference. For the both LDA and GGA calculations with \( U = 0 \), the NM-\( D_{3d} \) configuration was found to be the ground state and the NM-\( I_h \) configuration is the highest in energy, which is consistent with the JT structural instability of \( I_h \) discussed above. GGA predicts the larger stability of the non-magnetic NM-\( D_{3d} \) over the magnetic FM-\( I_h \). The stabilization energy of the NM-\( D_{3d} \) over FM-\( I_h \) and NM-\( I_h \) is 239 and 374 meV, in LDA, whereas 821 and 998 meV in GGA.
The relative order of stability among the different configurations remains the same even with $U = 2$ eV.

It is noted that the $D_{3d}$ structure is more stabilized over $I_h$ in GGA calculation than in LDA for both $U = 0$ and 2 eV; the stabilization energy is more than three times larger than in LDA. With a larger Coulomb interaction parameter, $U = 4$ eV, the total energy differences between FM-$I_h$ and NM-$D_{3d}$ are dramatically reduced for both LDA+$U$ and GGA+$U$ results. Indeed, in the case of LDA+$U$, the ground state is changed from the NM-$D_{3d}$ to the FM-$I_h$ configuration as shown in Fig. 3. This result implies that, when $U$ becomes large, the magnetic energy gain with an enhance exchange interaction can stabilize the symmetric $I_h$ structure against the Jahn-Teller distortion with a lower symmetry $D_{3d}$ structure. The strong on-site Coulomb interactions enhance the electron localization, which leads to the exchange energy gain thereby contributing to the stabilization of the undistorted structure. Figure 4 shows a charge density difference between $U = 2$ and $U = 0$ of FM-$I_h$. The blue and red colors represent the electron surplus regions of the $U = 2$ and $U = 0$ eV calculations, respectively. Though the magnitude of the charge difference is small, the difference plot of Fig. 4 demonstrates the tendency of electron localization at each carbon site, which arises from the electron correlation due to the on-site Coulomb interactions. The effect of the electron localization can affect the relatively enhanced exchange coupling among the degenerate HOMO states, and its magnitude seems to be comparable to that of the JT distortion. In Fig. 2 it is shown that the JT level spacing in Fig. 2(b) is comparable to that of the exchange splitting in Fig. 2(a). Since the JT distortion lifts up the orbital degeneracy of the HOMO states, the JT mechanism acts against the formation of magnetic moment in fullerene C$_{20}$. This result is another example demonstrating the discrepancy caused by the different XC energy functionals, and further is consistent with the previous studies [13, 14] which emphasized that the structural ground state depend on the type of XC energy functionals.

It is interesting to compare our LDA+$U$ and GGA+$U$ calculation results with the recent Hubbard-model-based study by Lin et al. [15]. Starting from an observation that the hopping parameter $t$ of the C$_{20}$ fullerene should be much smaller than that of C$_{60}$ but its on-site repulsion $U$ remains the same, which means that the ratio of $U/t$ is large, they assumed that electron correlations play an important role in this system and performed ED and QMC calculation for one-band Hubbard model parameterized by $U/t$,

$$H = -t \sum_{<i,j>,\sigma} (c_i^\dagger c_j + H.c) + U \sum_i n_i^\uparrow n_i^\downarrow.$$  

(5)
Their results predicted that the ground state of the $I_h$ structure changes from triplet to singlet at about $U/t \approx 4.10$, while the ground state of $D_{3d}$ evolves from the singlet (non-magnetic) state at $U = 0$ to a triplet state for $U/t$ larger than 0.5, and then transit to a singlet state again at $U/t \approx 4.19$. Those predictions based on the model analysis are in contradiction to our DFT calculations, where the FM state of the $I_h$ structure is always stable relative to the NM $I_h$ state and the JT distorted $D_{3d}$ structure prefers a non-magnetic ground state. The main difference between the Hubbard model approach and our DFT calculations lies on that our DFT calculations take account of the exchange coupling among the electrons occupying the HOMO states. The explicit treatment of the degenerate HOMO states is crucial since the energetic competition between the exchange coupling and the JT structural distortion is crucial for the degenerate states.

IV. CONCLUSION

We investigated the effect of on-site Coulomb correlations on the structural and magnetic properties of the fullerene C$_{20}$ by carrying out the LDA+$U$ and GGA+$U$ calculations. From the comparison of the total energies of the magnetic $I_h$ structure and the JT-distorted $D_{3d}$ structure for different values of the on-site Coulomb interaction $U$, we suggest that the exchange-coupling driven magnetic instability can possibly override the Jahn-Teller structural distortion at least for the value of $U = 4$ eV within the LDA+$U$ calculations. Considering the subtle dependence of the ground state properties of C$_{20}$ on the choice of XC-functional forms as well as the Hubbard model parameters, more elaborate calculations are required to resolve the physical picture for the ground state of the fullerene C$_{20}$, where the magnetic instability due to the Coulomb correlation effect competes with the structural distortion in the ‘superatom’ fullerene C$_{20}$.

Acknowledgments

This work was supported by a Korea Research Foundation (KRF) grant (MOEHRD KRF-2005-070-C00041). GK acknowledges the support by the post BK project. The calculations were carried out at the KISTI Supercomputing Center under the Supercomputing Application Focus Support
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The OpenMX DFT code used in this study are available on a web site (http://www.openmx-square.org/) in the constitution of the GNU General Public License.
TABLE I: LDA+U and GGA+U total energies (in meV unit) of the $I_h$ and $D_{3d}$ structures of C$_{20}$ with FM and NM spin configurations as a function of U. FM-$D_{3d}$ converges to be NM spin state in $U = 0, 2$ eV (see the text). The total energies are given relative to that of FM-$I_h$.

| XC-type | Symmetry | $U = 0$ eV | $U = 2$ eV | $U = 4$ eV |
|---------|----------|------------|------------|------------|
| LDA     | $I_h$ (FM) | 0          | 0          | 0          |
|         | $I_h$ (NM) | 135        | 217        | 566        |
|         | $D_{3d}$ (NM) | $-239$ | $-263$ | $33$ |
| GGA     | $I_h$ (FM) | 0          | 0          | 0          |
|         | $I_h$ (NM) | 177        | 259        | 795        |
|         | $D_{3d}$ (NM) | $-821$ | $-843$ | $-364$ |
FIG. 1: (Color online) Hückel’s molecular orbital levels for the highly symmetric $I_h$ structure and the Jahn-Teller distorted $D_{3d}$ structure of $C_{20}$. Up and down arrows indicate up and down spin electrons, respectively. The horizontal dashed line represents the Fermi level.
FIG. 2: (Color online) Total density-of-states (DOS) for (a) $I_h$ and (b) $D_{3d}$ structure $C_{20}$ fullerene. Up and down panels refer to the up-spin and down-spin states, and the dotted blue and solid red lines correspond to $U = 0$ and 2 eV, respectively. The DOS plots were drawn with the Gaussian broadening of 0.1 eV, and the Fermi energy is set at zero.
FIG. 3: (Color online) Total energy curves as a function of $U$. The calculated energies of NM-$I_h$ (dotted blue) and NM-$D_{3d}$ (solid red) are plotted with respect to that of FM-$I_h$ (dotted gray) in meV unit.
FIG. 4: (Color online) Iso-surface plot of the charge density difference of FM $I_h$ between $U = 0$ eV and $U = 2$ eV. Blue- and red-colored surfaces correspond to electron surplus regions for $U = 2$ eV and $U = 0$ eV, respectively, at the isovalue of $0.7 \times 10^{-3} \text{e} \cdot \text{Å}^{-3}$. 