# Hartree-Fock Dynamical Electron-Correlation Effects in $C_{60}$ after Laser Excitation

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In the static Hartree-Fock limit, the on-site electron-electron interaction has no effect on the electronic properties of $C_{60}$. But upon the laser excitation, the dynamical correlation effect appears. The time-dependent Hartree-Fock simulation through the Hubbard model shows that such an effect originates from the charge fluctuation, but an increase in the on-site electron-electron interaction suppresses the charge fluctuation and reduces the absorbed energy and the bond structure distortion.

The ever-growing ultrafast laser technology has been revolutionizing many aspects of the physics community by opening new frontiers such as attophysics [1] and femtomagnetism [2]. This technology has a unique capability, not commonly shared by other techniques, to snap shot the electron dynamics and to separate it from the dynamics of molecules, liquids, and solids. This presents an unprecedented opportunity to investigate various interactions on distinctive time scales. For instance, a typical electron-phonon interaction of 1 meV corresponds to 4 ps on the time scale; an electron-electron interaction of 1 eV corresponds to 4 fs. By probing dynamics on different time scales, one can predominantly target a specific interaction, or the time specificity. Such time specificity has already been employed in the literature to study superconductivities in high-$T_c$ superconductors and $MgB_2$ [3], to investigate the ultrafast spin dynamics in ferromagnets [2,4], to probe the spin coherence in semiconductors [5], and to reveal the intrinsic photoinduced isomerization in retinal molecules [6]. The ultrafast laser technology also greatly simplifies theoretical treatments by allowing one to focus on one particular interaction. For instance, in dynamics simulated by the semiconductor Bloch equation of motion [7], it is possible to deal with the electron-electron interactions on a fs time scale while leaving out or parametrizing the lattice effect.

Up to now, the most sophisticated calculations have been concentrated on semiconductors, but theories have substantially advanced our understanding of the electron-correlation effect in the time domain. First, the electron-electron interaction (EEI) is shown to be responsible for the difference between the nonlinear response of semiconductors and that of a noninteracting two-level system [8]. Second, EEI has been identified as the main dephasing source [9]. Third, it is found that the dynamical screened Coulomb potential builds up on the plasma oscillation period [10], which is confirmed by a recent experiment [11]. These and other studies reveal a fascinating picture of the ultrafast dynamics in semiconductors.

In this Letter, we employ the time-dependence Hartree-Fock (TDHF) approximation to investigate the dynamical electron-correlation effect in a $C_{60}$ cluster after laser excitation. The numerical simulation using the Hubbard model shows that although the effect comes from the charge fluctuation, an increase in the on-site EEI suppresses the charge fluctuation and reduces the total absorbed energy and bond distortions.

$C_{60}$ is a unique molecule with the $I_h$ point symmetry. Neutral $C_{60}$ has 60 $\pi$ electrons, where the interball hopping is much smaller than the on-ball hopping and therefore is neglected here. The Hamiltonian for the whole system can then be written as [12]

$$H_0 = -\sum_{i,j,\sigma} t_{ij}(c_{i,\sigma}^{\dagger}c_{j,\sigma} + \text{H.c.}) + \frac{K}{2}\sum_{i,j}(r_{ij} - d_0)^2$$
$$+ \frac{U}{2}\sum_{i\sigma}\left(n_{i\sigma} - \frac{1}{2}\right)\left(n_{i\bar{\sigma}} - \frac{1}{2}\right), \quad (1)$$

where all the electron operators are standard [13,14]. $t_{ij} = \tilde{t} - \alpha(|\mathbf{r}_i - \mathbf{r}_j| - d_0)$ is the hopping integral between nearest-neighbor atoms at $\mathbf{r}_i$ and $\mathbf{r}_j$, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Here $\tilde{t}$ is the average hopping constant, $\alpha$ is the electron-lattice coupling constant, and $d_0 = 1.54$ Å. The second term on the right-hand side of Eq. (1) is the lattice elastic energy, and $K$ is the spring constant. By fitting the energy gap and bond lengths, we have determined the above parameters as $\tilde{t} = 1.8$ eV, $\alpha = 3.5$ eV/Å, and $K = 30.0$ eV/Å$^2$ [12]. The last term in (1) is the electron-electron interaction $H'$, which under the Hartree-Fock approximation becomes

$$H'_{\text{HF}} = \frac{U}{2}\sum_{i\sigma}\left(\langle n_{i\sigma}\rangle - \frac{1}{2}\right)\left(n_{i\bar{\sigma}} - \frac{1}{2}\right). \quad (2)$$

Since $C_{60}$ is a half-filled system ($\langle n_{i\sigma}\rangle = 1/2$), in the static Hartree-Fock (SHF) limit Eq. (2) does not contribute to the original Hamiltonian. Thus any contribution from the on-site EEI in the Hartree-Fock limit must come from the dynamics.

The dynamical process is simulated by including the laser field, which is described by [4]

$$H_I = -e\sum_{i\sigma}\mathbf{E}(t)\cdot\mathbf{r}_i n_{i\sigma}, \quad (3)$$

where $|\mathbf{E}(t)| = A\cos[\omega(t-t_0)]\exp[-(t-t_0)^2/\tau^2]$ [4]. Here $A$, $\omega$, $\tau$, $e$, $t$, and $t_0$ are the field amplitude, laser frequency, pulse duration or width, electron charge, time, and time delay, respectively. To investigate the time-dependent ultrafast dynamics, we numerically solve the equation of motion for the electron density matrices [4],

$$-i\hbar\frac{\partial\rho_{ij}^{\sigma}}{\partial t} = \langle[\rho_{ij}^{\sigma}, H]\rangle$$

$$= \sum_k (t_{jk}\rho_{ik}^{\sigma} - t_{ki}\rho_{kj}^{\sigma}) + U\rho_{ij}^{\sigma}(\langle n_{j\bar\sigma}\rangle - \langle n_{i\bar\sigma}\rangle)$$

$$- e\rho_{ij}^{\sigma}\mathbf{E}(t)\cdot(\mathbf{r}_j - \mathbf{r}_i), \qquad (4)$$

where $H = H_0^{HF} + H_I$, the off-diagonal density matrix $\rho_{ij}^{\sigma} = \langle c_{i\sigma}^{\dagger}c_{j\sigma}\rangle$ characterizes the polarization on sites $i$ and $j$ and the diagonal matrix $\rho_{ii}^{\sigma} = \langle n_{i\sigma}\rangle = \langle c_{i\sigma}^{\dagger}c_{i\sigma}\rangle$ describes the on-site charge population. No damping term is introduced in (4). We treat the carbon atoms classically by solving the Newton dynamical equation [12,15].

Figure 1(a) shows the total absorbed energy $\Delta E$ [$\Delta E \equiv E(\text{excited}) - E(\text{unexcited})$] of the system (electron + lattice) as a function of time for two different interactions $U = 0$ and 2 eV. The total energy $E$ is computed as follows:

$$E = -\sum_{ij\sigma} t_{ij}\rho_{ij}^{\sigma} + \langle H_{HF}'\rangle + \frac{K}{2}\sum_{ij}(r_{ij}-d_0)^2 + \frac{1}{2}\sum_i mv_i^2, \qquad (5)$$

where the first two terms on the right-hand side are the total electronic energy, the last two terms are the lattice total energy, $m$ is the mass of carbon atoms, and $\{v_i\}$ is the velocity of atom $i$. Since the lowest transition from the highest occupied molecular orbital (HOMO) ($H_u$) to the lowest unoccupied molecular orbital (LUMO) ($T_{1u}$) is dipole forbidden, we tune the laser frequency to the first dipole-allowed transition from HOMO to LUMO + 1 ($T_{1g}$) at $\omega = 2.37$ eV [see the right inset of Fig. 1(a)]. We choose the laser time duration $\tau$ of 10 fs, the time delay $t_0 = 0$, and the laser polarization along the $z$ axis which perpendicularly goes through the center pentagon formed by five $a$ atoms [see the left inset in Fig. 1(a)]. From Fig. 1(a), one sees that upon the laser radiation, the system absorbs the energy sharply. The absorbed energy sensitively depends on $U$: An increase in $U$ from 0 to 2 eV reduces the absorbed energy from 4.54 to 3.15 eV, and the explicit dependence is shown in Fig. 1(b). The main reason for such a reduction is because an increase in $U$ reduces the transition matrix elements between HOMO and LUMO + 1 states. Thus for the same laser parameters, the number of excited electrons is reduced, which ultimately leads to a smaller $\Delta E$. A similar thing happens in the one-dimensional Hubbard model, where the optical conductivity $\sigma(\omega)$ obeys the $f$-sum rule [16], $\int_0^{\infty} d\omega\,\sigma(\omega) = -\langle T\rangle/2N$. And the kinetic energy $\langle T\rangle$ depends on $U$ as
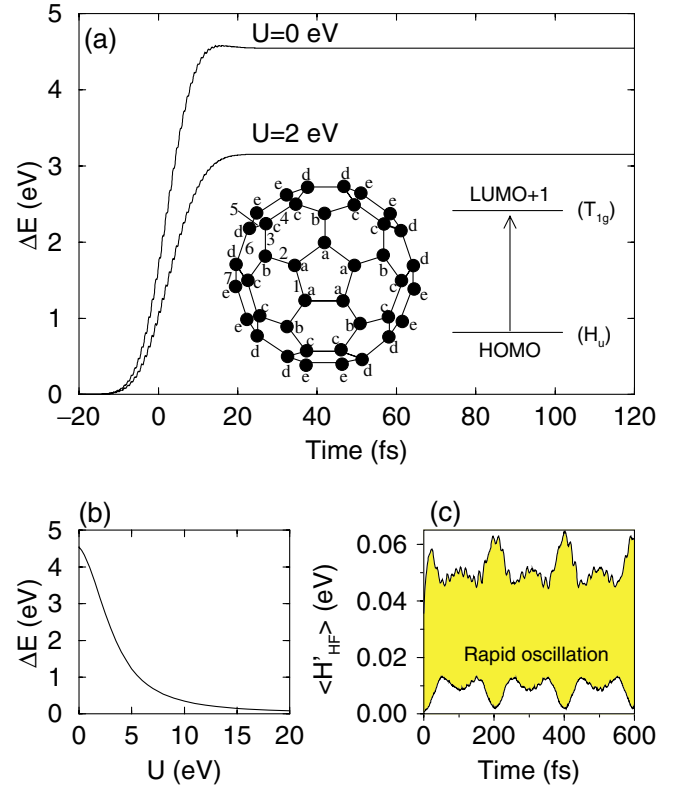


FIG. 1 (color online). (a) Absorbed energy $\Delta E$ versus time for $U = 0$ and 2 eV. Left inset: Schematic structure of $C_{60}$. Equivalent atoms are labeled with letters from $a$ to $e$, while the bonds are labeled by layer numbers $L$ from 1 (on the front pentagon) to 7 (in the equatorial region). Only one representative bond in each layer is labeled by $L$. There are six symmetric layers from 8 to 13 on the back (not shown). In the unexcited $C_{60}$, bonds in layers 1, 3, 5, and 6 are single bonds while bonds in 2, 4, and 7 are double bonds. The electric field polarization is chosen along the $z$ axis which perpendicularly goes through the center of the pentagon formed by five $a$ atoms. (b) Dependence of $\Delta E$ on the on-site electron-electron interaction. (c) The expectation value of the on-site electron-electron term $\langle H_{HF}'\rangle$ versus time. The shaded area represents many rapid oscillations.

$$-\langle T\rangle/4Nt \sim (1 - 0.213\,58U^2/16)/\pi, \quad \text{for } U \ll 1; \quad (6)$$

$$\sim \left[\frac{1}{8}\ln 2 - \left(\frac{3}{64}\right)^2\zeta(3)U^{-2}\right]U^{-1}, \quad \text{for a large } U, \quad (7)$$

where $\zeta(x)$ is the Riemann zeta function. Since $\langle T\rangle$ decreases upon an increase in $U$, the optical response is suppressed. The good agreement between our numerical results and the analytical solution in the Hubbard model suggests that TDHF, though approximate, fairly accurately describes the electron-correlation effects. This is not surprising as the dynamical mean-field approximation [17], based on the same principle as TDHF, is able to account for electron-correlation effects even in transition-metal oxides and high-$T_c$ materials.

This initial success gives us confidence to investigate the dynamical electron-correlation effects in such a molecular system. In Fig. 1(c), we show the change of the

Hartree-Fock EEI term $\langle H'_{HF} \rangle$ versus time up to 600 fs, where the shaded area represents many rapid oscillations. The term $\langle H'_{HF} \rangle = \frac{U}{2} \sum_{i\sigma} (\langle n_{i\sigma} \rangle - \frac{1}{2})(\langle n_{i\bar{\sigma}} \rangle - \frac{1}{2})$ is exactly zero in the SHF limit, but upon laser excitation, it is not. Thus, physically $\langle H'_{HF} \rangle$ can be considered as dynamical correlated correction energy. We choose $U = 2$ eV. The energy change exhibits both collective (envelope) and individual (shaded area) oscillations. The collective one has two major components with the same period of about 200 fs, but they are from different charge fluctuations. We find that the smaller component has the sole charge contributions from $d$ and $e$ atoms around the equatorial region and their symmetric atoms on the back [see the left inset in Fig. 1(a)], but the large component has the joint contributions from $c$, $d$, and $e$ atoms and their symmetric counterparts on the back (not shown), which explains why its magnitude is larger.

From Eq. (2), it is clear that the change in $\langle H'_{HF} \rangle$ is proportional to the on-site charge fluctuation $\chi_0 \equiv \sum_{i\sigma} (\langle n_{i\sigma} \rangle - \frac{1}{2})(\langle n_{i\bar{\sigma}} \rangle - \frac{1}{2})$. It is well known that the electron correlation has a significant effect on the charge fluctuation. In Fig. 2(a), we show $\chi_0$ for $U = 0$ and 2 eV. At $U = 0$ eV, we again see that there are two different oscillations with different amplitudes. The peak-to-peak amplitude for the small oscillation is about 0.04 while for the big one it is 0.07. When we increase $U$ to 2 eV, the large peak sharply reduces to 0.03, and the small peak becomes even smaller. This is consistent with the nature of the on-site EEI: A strong $U$ suppresses the charge fluctuation.
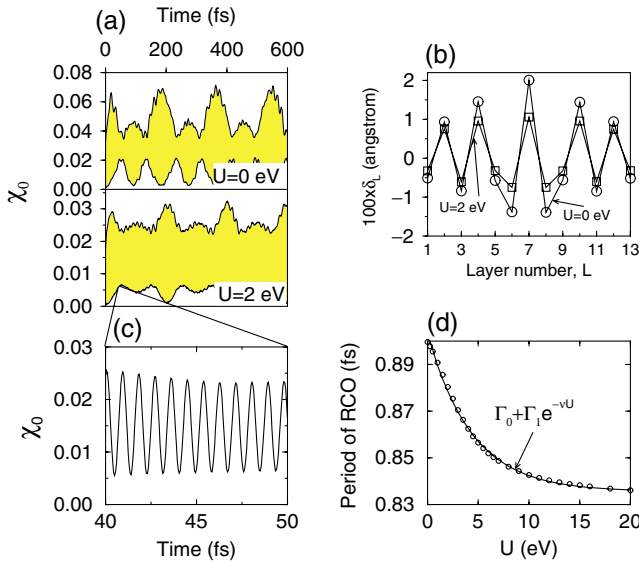
Our calculation shows that when $U$ is larger than 4 eV, those peaks are almost washed out completely. This demonstrates that TDHF catches the dynamical aspect of the electron-correlation effect by self-consistently correcting the charge fluctuation.

The electron correlation affects not only the charge fluctuation but also the bond structure of $C_{60}$. Figure 2(b) displays the maximum bond length deviations $\delta_L$ from their respective original lengths versus bond layer number $L$ for $U = 0$ and 2 eV. These layer numbers are labeled starting from the bonds in the center pentagon [see the left inset of Fig. 1(a)]. For instance, layer 1 refers to the bonds connecting $a$ atoms, while layer 2 denotes the bonds between $a$ and $b$ atoms (or hexagons) and layer 3 is between $b$ and $c$ atoms, and so on. We only label one representative bond in each layer by numbers from 1 to 7. Symmetric layers on the back are labeled from 8 (adjacent to layer 7) to 13 (on the back pentagon just behind the above front center pentagon). In the unexcited $C_{60}$, there are two different kinds of bonds: single bonds are in layers 1, 3, 5, and 6 and double bonds in layers 2, 4, and 7. In the excited $C_{60}$, there are seven different bonds [see Fig. 2(b)]. After the excitation, those short bonds become longer and the longer bonds become shorter. The change is not uniform and the maximum deviation is in layer 7. For $U = 0$ eV, the maximum bond distortion $\delta_L$ is 0.02 Å. When we increase $U$ to 2 eV, the maximal $\delta_L$ is reduced to 0.01 Å. From the above, we have seen that the on-site EEI suppresses the charge fluctuation, and now through the electron-lattice coupling it reduces the lattice distortion. These dynamical correlation effects are linked to charge oscillations.

In order to examine those rapid charge oscillations (RCO) [see the shaded areas in Figs. 1(c) and 2(a)], in Fig. 2(c) we enlarge a small portion of those rapid oscillations for $U = 2$ eV from 40 to 50 fs. From Eq. (4), we notice that the period of the charge density is determined by the hopping integral, the EEI term, and the external field. If we combine the last two terms in (4) together, the common factor of $\rho^\sigma_{ij}$ is just the renormalized Rabi energy $\hbar \Omega^{ij}_R$ ($\Omega^{ij}_R$ is the frequency) though in the position space,

$$\hbar \Omega^{ij}_R = e\mathbf{E}(t) \cdot (\mathbf{r}_j - \mathbf{r}_i) - U(\langle n_{j\bar{\sigma}} \rangle - \langle n_{i\bar{\sigma}} \rangle), \quad (8)$$

where the first term is the normal Rabi energy and the second term is from the on-site EEI. After the laser field is over, the Rabi frequency exclusively depends on the electron-electron interaction $U$. Now, if we transform the $U$ term into the state space, all the energy levels obtained at the bare hopping-integral limit become renormalized with a time-dependent contribution from the $U$ term. Consequently, the rapid period $\Gamma_{RCO}$ depends on both $U$ and the hopping integral. In Fig. 2(d), we show the dependence on $U$. If the EEI is small, the RCO period linearly depends on the EEI, which is just the first part of Fig. 2(d). When $U$ becomes larger, the period decreases exponentially [see Fig. 2(d)]. The explicit dependence on



FIG. 2 (color online). (a) The charge fluctuation $\chi_0$ versus time for two different on-site $U = 0$ (top panel) and 2 eV (bottom panel). (b) Dependence of lattice bond length deviation $\delta_L$ on $U$. The circles are for $U = 0$ eV while the boxes for $U = 2$ eV. The layer numbers $L$ refer to those numbers in the left inset of Fig. 1(a). (c) Enlarged $\chi_0$ from 40 to 50 fs for $U = 2$ eV. (d) The period of the rapid oscillations in $\Delta E$ decreases as $U$ increases.

$U$ can be fitted to

$$\Gamma_{RCO} = \Gamma_0 + \Gamma_1 \exp(-\nu U), \qquad (9)$$

where $\Gamma_0 = 0.84$ fs, $\Gamma_1 = 0.068$ fs, and $\nu = 0.22/\text{eV}$.

However, experimentally it has been challenging to probe such a fast charge oscillation. The current pulse duration is about $4-6$ fs, delivered by a Ti:sapphire laser at 800 nm, but the laser with such a duration has already opened an exciting field of femtochemistry [18]. Subsequent experimental developments are truly remarkable. A sub-6-fs pulse was demonstrated by frequency doubling with quasi-phase-matching gratings [19]. Femtosecond x rays from the synchrotron source at the Advanced Light Source at Lawrence Berkeley National Laboratory catch great attention [20] and have high flux and repetition rate though their pulse duration is still too long. The latest breakthrough in the attosecond physics [1] demonstrates the possibility to probe dynamics on the attosecond time scale. The attotechnology might ultimately enable us to ''see'' these oscillations in real time and directly ''probe'' the effects of the electron-electron interaction experimentally.

In conclusion, within the time-dependent Hartree-Fock approximation we investigate the dynamical correlation effect in $C_{60}$ after the laser excitation. The on-site electron-electron interaction reduces the absorbed energy and suppresses the charge fluctuation which is the precondition to see the dynamical correlation effect. The on-site interaction reduces the bond distortion in $C_{60}$ and shortens the period of those rapid oscillations.

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