Manifestation of electron-electron interactions in time-resolved ultrafast pump-probe spectroscopy in C_{60}: Theory

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The electron-electron interaction (EEI) is at the core of modern physics from high-temperature superconductivity to giant magnetoresistance. Nanostructures, in general, and C_{60}, in particular, open a new frontier for the study of the electron correlation effect in quasi-zero-dimensional materials. Here, a direct investigation of the time-resolved pump-probe signal in C_{60} shows that the on-site electron-electron interaction manifests itself in two aspects in the early stage of ultrashort laser excitation. First, it pushes the signal peak to an earlier time delay for below-resonance excitation and narrows the peak-time change with probe detuning. Second, it shortens the quasiparticle lifetime and, if the interaction is strong enough, it diminishes the spike in the lifetime at resonance. These features are detectable experimentally, and the findings here suggest a different route to detect dynamical EEI in nanostructures.

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I. INTRODUCTION

When a system is exposed to a laser field, a single-particle excitation is launched. Such an excitation with a long lifetime is called a quasiparticle,[1] whose lifetime contains crucial information about the electron-electron interaction (EEI) and other interactions of the system.[1] It is this fundamental concept that has attracted much theoretical investigation over the past half-century. The lifetime not only can be computed theoretically but can be probed experimentally using ultrafast laser pulses[2] which, with pulse durations as short as a few femtoseconds, can time resolve the dynamics of quasiparticles. Significant insight into quasiparticle excitations is revealed in solids.[2] Nanostructures such as fullerenes and nanotubes[3] present an unprecedented opportunity to explore the correlation effect, where the cluster size, shape, geometry, and dimensionality can be manipulated systematically.

However, a major experimental difficulty in nanostructures is to characterize their size, geometry, and shape.[4] We choose C_{60} as our model system, where C_{60} samples have purity over 99.99%, have a well-defined molecular structure, and are free from the above difficulty. Besides this apparent advantage, C_{60} has attractive structural, electronic, and optical properties. Alkali-doped C_{60} is a superconductor with transition temperature of 18 K in K_3C_{60} and of 33 K in Rb_3C_{60}.[5] Tetrakis-dimethylamino-ethylene C_{60} exhibits the highest magnetic-ordering temperature of any organic magnet.[6] Its high π-electron delocalization renders a large nonlinear optical susceptibility over 10^{-12} esu at off resonance[7] and an optical response time shorter than a few hundred femtoseconds. It holds promise for an ultrafast photodiode[8] and optical switching. This motivates intense experimental[9] and theoretical[10,11] investigations on the vibrational[12] and electronic[13] excitations in C_{60}. The investigation of the dynamical processes on an ultrafast time scale will give much needed insight into the role of EEI on earlier times of quasiparticle excitation in this nanosystem.

In this paper, we show in C_{60} that the on-site electron-electron interaction manifests itself in two distinctive aspects in ultrafast pump-probe spectroscopy. First, it shifts the pump-probe signal peak to an earlier time delay and narrows the peak-time dispersion with the probe detuning. Second, it reduces the quasiparticle lifetime and, if the interaction strength is strong enough, it diminishes the spike in the lifetime at resonance. The first feature can be probed by off-resonantly exciting the system with laser energy of 0.05 eV below the resonance and with pulse duration of 10 fs. The second feature can be revealed with laser energy detuning of 0.1 eV around the resonance. We establish a simple relation between the lifetime and on-site EEI strength, which presents an opportunity to directly measure the EEI strength experimentally.

The rest of the paper is arranged as follows. In Sec. II, we present our theoretical formalism. The results and accompanying discussion of the pump-probe signal peak time and the quasiparticle lifetime are presented in Secs. III A and III B, respectively. We conclude our paper in Sec. IV.

II. FORMALISM

In a typical time-resolved pump-probe experiment, a pump pulse of frequency ω_1 and wave vector $\vec{k}_1$ impinges on C_{60}, and after a time delay T, a probe pulse of ω_2 and $\vec{k}_2$ probes the change left behind by the pump pulse. To avoid the artificial interference effect, their polarizations are taken as perpendicular to each other. The inset of Fig. 1(a) schematically shows the experimental geometry. The signal, which propagates along the $\vec{k}_1-\vec{k}_1+\vec{k}_2$ direction, is detected, and its intensity is proportional to[14]

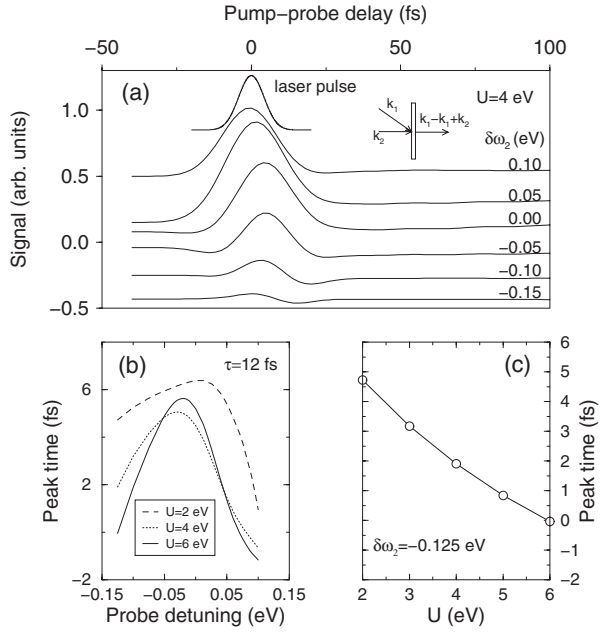

FIG. 1. (a) Pump-probe signal as a function of the time delay between the pump and the probe for the probe detuning from $\delta\omega_2 = -0.15$ to 0.10 eV. The pump energy is 0.1 eV below E_0. A schematic of the pump-probe experimental transmission geometry is shown in the upper right inset. Although the pump pulse also transmits through the sample (the vertical bar), only the signal along the direction $k_1 - k_1 + k_2$ is probed. The pulse duration for both the probe and pump pulses is 12 fs. $A_1 = 0.05$ V/Å and $A_2 = 0.01$ V/Å. All the curves are vertically shifted for a better view. (b) Peak time as a function of the probe detuning for $U = 2$ eV (dashed line), $U = 4$ eV (dotted line), and $U = 6$ eV (solid line). (c) Peak time as a function of U at probe detuning $\delta\omega_2 = -0.125$ eV.

$$I(T) \propto \omega_2 \,\mathrm{Im} \int_{-\infty}^{\infty} \vec{E}_2^*(t) \cdot \vec{P}_{\vec{k}_2}^{(3)}(t) dt, \tag{1}$$

where $\vec{E}_2(t)$ is the probe field's envelope function. $\vec{P}_{\vec{k}_2}^{(3)}(t)$, the third-order polarization propagating along the k_2 direction, is computed from $\vec{P}_{\vec{k}_2}^{(3)}(t) = \Sigma_i \rho_{i,i;\vec{k}_2}^{(3)} \vec{r}_i$, where $\vec{r}_i$ is the ith electron position and $\rho_{\vec{k}_2}^{(3)}$ is the third-order electron density matrix along the $\vec{k}_2$ direction. As it can be seen from Eq. (1), for each time delay, one has to integrate over time, which is the most time consuming part.

The time evolution of the density matrix is computed by solving the Liouville equation,[10,13,15]

$$i\hbar \dot{\rho}_{ij} = [H_0 + H_I, \rho_{ij}]. \tag{2}$$

The unperturbed C_{60} Hamiltonian is

$$H_0 = -\sum_{\langle ij\rangle,\sigma} t_{ij}(c_{i,\sigma}^{\dagger} c_{j,\sigma} + \mathrm{H.c.}) + U \sum_i \left(n_{i\uparrow} - \frac{1}{2}\right)\left(n_{i\downarrow} - \frac{1}{2}\right), \tag{3}$$

where $c_{i,\sigma}^{\dagger}$ ($c_{i,\sigma}$) is the electron creation (annihilation) operator with spin σ, $n_{i\sigma} = c_{i,\sigma}^{\dagger} c_{i,\sigma}$, t_{ij} is the hopping integral,[13] and the last term is the on-site electron-electron interaction with strength U. Only 60 π electrons are included and one for each atom. The interaction Hamiltonian between the laser field and the system is $H_I = [\vec{F}_1(t) + \vec{F}_2(t+T)] \cdot \Sigma_{i\sigma} n_{i\sigma} \vec{r}_i$, where T is the probe pulse time delay with respect to the pump, and the pump/probe field is $\vec{F}_{1/2}(t) = \hat{e}_{1/2} E_{1/2}(t)(e^{i\vec{k}_{1/2}\cdot\vec{r} - i\omega_{1/2}t} + \mathrm{H.c.})$. $\hat{e}_{1/2}$ is the laser polarization, $\vec{r}$ is the position vector of the electric field, and the laser envelope function is $E_{1/2}(t) = A_{1/2} e^{-t^2/\tau_{1/2}^2}$, where $A_{1/2}$ is the field strength and $\tau_{1/2}$ is the pump/probe pulse duration. Under the dipole approximation [replacing $\exp(i\vec{k}\cdot\vec{r})$ in $\vec{F}$ by 1], the spatial dependence of the electric field does not appear in H_I. We still keep $\exp(i\vec{k}\cdot\vec{r})$ in $\vec{F}$ merely because we need it to identify different propagation directions as will become clear below.

The signal probed experimentally along the direction of $\vec{k}_q$ is proportional to $\rho^{(q)} \exp(i\vec{k}_q \cdot r - i\omega_q t)$, but solving the Liouville equation only gives the total density. In order to distinguish different directions, we express the total density matrix element as

$$\rho_{ij} = \sum_{nm} \rho_{ij}^{(n|m)} \exp(in\vec{k}_1 \cdot \vec{r} - in\omega_1 t + im\vec{k}_2 \cdot \vec{r} - im\omega_2 t), \tag{4}$$

where $\rho_{ij}^{(n|m)}$ represents the density matrix along the $(n\vec{k}_1 + m\vec{k}_2)$ direction and carries the electron position indices i, j. $\vec{r}$ may take i, j but since k is very small in the visible light region, both $\exp(in\vec{k}_1 \cdot \vec{r})$ and $\exp(im\vec{k}_2 \cdot \vec{r})$ are close to 1 and may be removed. However, we still keep them there simply because we need them for the propagation direction purpose.

To see how this works, let us substitute Eq. (4) into Eq. (2) and treat the electron-electron interaction term within the time-dependent Hartree-Fock approximation.[13] The left-hand side of the Liouville equation becomes[16]

$$\sum_{nm} [i\hbar \dot{\rho}_{ij}^{(n|m)} + \hbar(n\omega_1 + m\omega_2)\rho_{ij}^{(n|m)}] e^{i(n\vec{k}_1 + m\vec{k}_2)\cdot\vec{r} - i(n\omega_1 + m\omega_2)t}. \tag{5}$$

On the right-hand side of Eq. (2), $[H_0, \rho_{ij}]$ is straightforward, so we focus on $[H_I, \rho_{ij}]$ and use the pump field $\vec{F}_1$ as an example. Since the formulas are too lengthy, we only show those terms, such as $\vec{F}_1 \rho_{ij}$, that are most relevant to the propagation direction. We first rewrite $\vec{F}_1 = \vec{E}_1 e^{i\vec{k}_1\cdot\vec{r} - i\omega_1 t} + \vec{E}_1^* e^{-i\vec{k}_1\cdot\vec{r} + i\omega_1 t}$, where $\vec{E}_1 = \hat{e}_1 E_1(t)$. Then, we have

$$\vec{F}_1 \rho_{ij} = \sum_{nm} \rho_{ij}^{(n|m)} (\vec{E}_1 e^{i(n+1)\vec{k}_1\cdot\vec{r} - i(n+1)\omega_1 t + im\vec{k}_2\cdot\vec{r} - im\omega_2 t} + \vec{E}_1^* e^{i(n-1)\vec{k}_1\cdot\vec{r} - i(n-1)\omega_1 t + im\vec{k}_2\cdot\vec{r} - im\omega_2 t}), \tag{6}$$

which can be simplified by factoring out the common phase factor,

$$\vec{F}_1 \rho_{ij} = \sum_{nm} [\rho_{ij}^{(n-1|m)} \vec{E}_1 + \rho_{ij}^{(n+1|m)} \vec{E}_1^*] e^{in\vec{k}_1\cdot\vec{r} - in\omega_1 t + im\vec{k}_2\cdot\vec{r} - im\omega_2 t}. \tag{7}$$

Without loss of generality, by equating coefficients with the same phase factor of Eq. (5) and terms like those in Eq. (7), we can write

$$
\begin{aligned}
i\hbar\dot{\rho}_{ij}^{(n|m)} = &-\hbar(n\omega_1 + m\omega_2)\rho_{ij}^{(n|m)} + \sum_l (t_{il}\rho_{lj}^{(n|m)} - \rho_{il}^{(n|m)}t_{lj}) \\
&+ \vec{E}_1 \cdot (\vec{r}_i - \vec{r}_j)\rho_{ij}^{(n-1|m)} + \vec{E}_1^* \cdot (\vec{r}_i - \vec{r}_j)\rho_{ij}^{(n+1|m)} \\
&+ \vec{E}_2 \cdot (\vec{r}_i - \vec{r}_j)\rho_{ij}^{(n|m-1)} + \vec{E}_2^* \cdot (\vec{r}_i - \vec{r}_j)\rho_{ij}^{(n|m+1)} \\
&+ U\sum_{\alpha,\beta} [\rho_{ii}^{(n-\alpha|m-\beta)} - \rho_{jj}^{(n-\alpha|m-\beta)}]\rho_{ij}^{(\alpha|\beta)}. \qquad (8)
\end{aligned}
$$

Phase factors such as $e^{in\vec{k}_1\cdot\vec{r}}$ do not appear in the above equation explicitly. However, they do help us identify a correct propagation direction in Eq. (7), as does the phase factor in the field. This explains why we should include those factors even though the dipole approximation is used. As one can see from Eq. (8), the time-dependent Hartree-Fock approximation is used in our calculation. While it is desirable to have a higher-level calculation, it is very time consuming, as mentioned before, and this approximation provides a good alternative.[17,18]

With this generic expression, we can now compute the signal. The above $\rho_{\vec{k}_2}^{(3)}$ is $\rho^{(1-1|1)}$ or $\rho^{(0|1)}$ (third order) in the current notation. We caution here that this component, which interacts with the pump field twice and probe once, does not come out of the generic equation (8) automatically. Thus, one has to select the relevant terms carefully according to the experimental techniques, such as pump-probe versus degenerate four-wave mixing. We will show an example below. The third-order $\rho^{(0|1)}$ should not be confused with the first-order $\rho^{(0|1)}$, since the latter only interacts with the field once. In real calculations, we normally sort them out first before we write the code. Since the pump-probe signal must be approximately proportional to the $|\vec{F}_1|^2|\vec{F}_2|^2$, this provides an ultimate check on our calculation.[16] Our result is indeed consistent with this prediction.

In the following, we use the third order as an example to show how one can get an expression for $\rho^{(0|1)}$ from Eq. (8). The first and second terms have the same $(n|m)$, so both are kept. For the pump-probe measurement, $n=0$ and $m=1$. $m=1$ means that the signal interacts with the probe field only once, so that we keep just terms for the interaction with the probe field only once. As a result, the sixth term in Eq. (8), which interacts with the probe field twice, is left out. Only one term (the fifth term) interacting with the probe field is kept.

It is worthwhile to discuss n in detail. In fact, $n=0$ should be written as $n=1-1$ to be clear. This means that the system interacts with the pump field k_1 twice, where one is emission and the other is absorption. Since there are two possible orders—emission first or absorption first—two terms (terms 3 and 4) appear in Eq. (8), both of which are kept.

The above selection scheme applies in other techniques. These considerations lead to

$$
\begin{aligned}
i\hbar\dot{\rho}_{ij}^{(0|1)} = &-\hbar\omega_2\rho_{ij}^{(0|1)} + \sum_l (t_{li}\rho_{lj}^{(0|1)} - t_{lj}\rho_{il}^{(0|1)}) \\
&+ \vec{F}_1 \cdot (\vec{r}_i - \vec{r}_j)\rho_{ij}^{(-1|1)} \\
&+ \vec{F}_1^* \cdot (\vec{r}_i - \vec{r}_j)\rho_{ij}^{(1|1)} + \vec{F}_2 \cdot (\vec{r}_i - \vec{r}_j)\rho_{ij}^{(0|0)} \\
&+ U\sum_{\alpha\beta} [\rho_{ii}^{(-\alpha|1-\beta)} - \rho_{jj}^{(-\alpha|1-\beta)}]\rho_{ij}^{(\alpha|\beta)}, \qquad (9)
\end{aligned}
$$

where the last term is the EEI contribution, and α and β are chosen such that the density products contain only terms interacting with the pump field twice and probe once. Specifically, the terms in the last summation that we omit are $\rho^{(0|2)}\rho^{(0|-1)}$ and $\rho^{(0|-1)}\rho^{(0|2)}$, since both interact with the probe field three times, which are not probed experimentally. We also note that $\rho_{ij}^{(0|0)}$ in the fifth term of Eq. (9) is not a zero-order density matrix. Instead, it is $\rho_{ij}^{(1-1|0)}$ which represents the interaction with the pump field twice.

The initial condition for zero-order density matrices is computed at the Hartree-Fock limit long before the first pulse arrives. All the lower-order equations are solved self-consistently together with Eq. (9), in a similar fashion as $\rho^{(0|1)}$. Once we find $\rho^{(0|1)}$, we directly compute $\vec{P}_{\vec{k}_2}^{(3)}(t)$. Finally, we integrate Eq. (1) over time to get the signal $I(T)$. For each time delay, we solve a set of differential equations of ρ. This gives the signal as a function of time delay, which can be measured experimentally.

III. RESULTS AND DISCUSSION

A. Peak time of the pump-probe signal

In C_{60}, the first dipole-allowed transition is between the highest occupied molecular orbital and the lowest unoccupied molecular orbital+1, whose resonant transition energy E_0 is 2.76 eV for the noninteracting case. For convenience, in the following, all the pump and probe energies are referenced to E_0. For interacting cases, the resonance energy is shifted to a value slightly larger than E_0. We start with $U=4$ eV, where the shift toward the high-energy side is 0.05 eV. We pump the system off resonantly with $\delta\omega_1=\omega_1-E_0=-0.1$ eV. The probe detuning $\delta\omega_2=\omega_2-E_0$ changes from −0.15 to 0.10 eV. Both the pump and probe durations are $\tau_{1/2}=12$ fs; the pump and probe field strengths are $A_1=0.05$ V/Å and $A_2=0.01$ V/Å, respectively. Figure 1(a) shows a pump-probe signal change as a function of the time delay between the pump and probe pulses for six probe detunings. We see that the signal increases quickly when the pump and probe pulses overlap, after which it decays. As the probe detuning increases, the signal peaks at different delay times, shifting from a positive peak time at $\delta\omega_2=-0.15$ eV to a negative peak time at $\delta\omega_2=0.10$ eV. In four-wave mixing spectroscopy, no signal appears at negative delays in a noninteracting two-level system, and in semiconductors the signal at negative delays is an indication of the EEI effect.[19] In pump-probe spectroscopy, due to the finite pulse width, there are always signals at negative time delay, but whether or not the signal peak-time change would be an indication of the EEI is an interesting but largely unexplored topic in C_{60}.

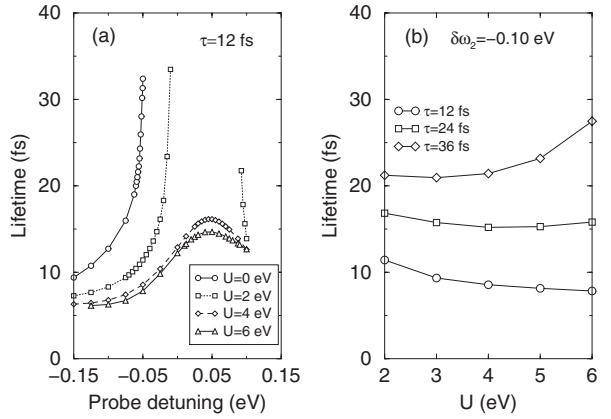

FIG. 2. (a) Dependence of the lifetime on the probe detuning for $U=0-6$ eV, where $\tau_{1/2}=12$ fs, $A_1=0.05$ V/Å, and $A_2=0.01$ V/Å. (b) Dependence of the lifetime on U for pulse durations $\tau=12$ fs (circles), 24 fs (boxes), and 36 fs (diamonds). Here, the probe detuning is fixed at −0.10 eV.

Figure 1(b) compares the peak times for three on-site interactions, which bracket the 2–6 eV range of possible values of U in C_{60}. Here, the probe detuning scans from $\delta\omega_2=-0.15$ to 0.10 eV. The data indeed confirm our observation in Fig. 1(a) that the peak time systematically disperses with the probe detuning. More importantly, the dispersion shows a strong dependence on U. At $U=2$ eV, the dispersion is very broad, which means that the pump-probe signal peak change is very gradual with $\delta\omega_2$. When U is increased to 4 eV, the dispersion becomes narrower. This trend persists even for $U=6$ eV. This is the first indication of EEI, which can be directly measured experimentally. We also notice that for $\delta\omega_2$ below resonance, there is a simple monotonic dependence of the peak time on U. Figure 1(c) shows that at $\delta\omega_2=-0.125$ eV, the peak time decreases from 5 to 0 fs by increasing $U=2$ eV to $U=6$ eV. This demonstrates that the peak time contains crucial information about EEI, where the on-site electron-electron interaction manifests itself by pushing the signal peak to an earlier delay time and narrowing the peak-time dispersion with $\delta\omega_2$.

B. Electron-electron interaction effect on the quasiparticle lifetime

The probe detuning affects not only the peak time but also the lifetime of the quasiparticle excitation, which is defined here as the time at $1/e$ of the signal peak amplitude. We systematically investigate EEI by changing U from 0 to 6 eV. We first focus on the results of the noninteracting case [see the open circles in Fig. 2(a)], where the resonance is precisely at $\delta\omega_2=0$. As the probe energy increases toward the resonance, the lifetime increases sharply and diverges, though naturally, on a much longer time scale, the lifetime does not diverge and is set by the electron-phonon and phonon-phonon interactions, which are not considered here. Note that although we scan across the probe energy from $\delta\omega_2=-0.15$ to 0.1 eV, the pump-probe signals above the resonance do not drop to $1/e$ of the signal maximum, and consequently no data points are shown. By turning on EEI to $U=2$ eV, the lifetime below the resonance behaves similarly to the noninteracting case, but for the above-resonance excitation, the signal does show a finite lifetime [see the open squares on the right side of the resonance in Fig. 2(a)]. Further increase in U to 4 eV diminishes the lifetime divergence at the resonance [see the diamonds in Fig. 2(a)]. Such pronounced lifetime reduction is a manifestation of EEI, where the electron-electron interaction suppresses the charge fluctuation and shortens the lifetime of the quasiparticle excitation. For larger U, the change becomes even more pronounced. For instance, at $U=6$ eV, the suppression of the lifetime becomes even greater [see the triangles in Fig. 2(a)].

The reason why EEI plays such a critical role[20] in the quasiparticle lifetime can be understood from the last term in Eq. (9), where $\rho_{ii}^{(-\alpha|1-\beta)}$ and $\rho_{jj}^{(-\alpha|1-\beta)}$ both propagate along the $[-\alpha\vec{k}_1+(1-\beta)\vec{k}_2]$ direction but belong to different sites i and j. If they take quite different values, then the U term contributes strongly and suppresses the charge excitation, a built-in self-consistency. This happens when the system is excited resonantly, which is why the resonant lifetime is sharply reduced and the divergence is strongly suppressed. On the other hand, if $\rho_{ii}^{(-\alpha|1-\beta)}$ and $\rho_{jj}^{(-\alpha|1-\beta)}$ are roughly equal, the U term cannot contribute strongly. This happens when the system is excited off resonantly. As a result, we see no significant difference between the lifetimes of the noninteracting and interacting cases for the off-resonant excitation. Let us consider probing these distinctive features of EEI effects experimentally.

In experiments, the relevant parameters include the laser field strength, pulse wavelength, and duration, which we now investigate one by one. We find that a moderate field strength around 0.05 V/Å is enough to reveal the correlation effect, and too strong a laser often induces high excitation which blurs the effect of EEI. The pump laser wavelength has a significant effect on the final results. The optimal laser energy is about 0.1–0.2 eV below the resonance, which balances the signal-to-noise ratio and avoids high excitation, as mentioned above. Such a small change in the laser energy is desirable experimentally.[9,21] Probably, the most critical parameter is the laser pulse duration. Figure 2(b) shows the lifetime change as a function of U from 2 to 6 eV. One sees that when the pulse duration is as short as 12 fs, the lifetime decreases with U, consistent with the theoretical prediction, but when the duration is 36 fs, due to multiple excitations, the lifetime now increases with U. This points out the necessity of ultrashort pulses, which are available in many research laboratories.[9,22] Recent high-harmonic generation[23] can generate pulses with duration on the order of a few hundred attoseconds. Since there is a simple dependence of the lifetime on U for shorter pulses, future experiments can directly test our theoretical prediction, and importantly, directly measure the magnitude of U. As many other nanostructures share similar features with C_{60}, this suggests a different route to probe the EEI strength experimentally by directly measuring the lifetime dependence on probe detuning and comparing it to the theoretical prediction.[24]

IV. CONCLUSION

We directly compute the time-resolved pump-probe signal in C_{60} under the influence of ultrafast laser pulses. We show

that EEI manifests itself by shifting the peak time to an earlier time delay, narrowing the peak-time dispersion with the probe detuning, and strongly suppressing the lifetime. If the EEI strength is strong enough, the lifetime divergence will disappear. This is a pure effect of EEI, where the suppression of the charge excitation is from the on-site electron-electron interaction. For an ultrafast laser pulse, there is a simple relation between the lifetime and electron-electron interaction strength. These results are detectable experimentally, as lasers as short as 10 fs are already accessible to many research groups. In fact, similar experiments have been done for nanotubes[3] and other nanostructures. C_{60} is a much cleaner example for experimental exploration due to its well-characterized structural, electronic, and optical properties. An experimental realization of our findings paves the way to developing a sensitive tool to probe the strength of EEI in nanostructures.

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[17] It is certainly desirable to perform a high-level theoretical calculation on the dynamical process, and there are three basic reasons that make the dynamical Hartree-Fock approximation very attractive. First, our problem is not only about the ground state but also about the excited states, where the total Hilbert space for C_{60} is 4^{60}. The calculation exhausts almost all the existing computing facilities. Since the pump-probe optical response involves three coupled equations for each pair of states i,j, this means that one has to solve $3\times 4^{60}\times 2$ (real and imaginary parts) differential equations for each time point. For each time delay, there are about 50 000 time points to get one signal point that is probed experimentally. To the best of our knowledge, no such study has ever been performed. Second, the dynamical Hartree-Fock approximation is a well-established formalism that has been used by many research groups for molecules and semiconductors. The beauty of this is that it takes self-consistency into account naturally, and for a moderate system, it is a very practical method as demonstrated here, which is the reason that the dynamical mean field theory attracts so much attention from the high-T_c communities. What is missing is the high-order correlation effect. Third, the pump-probe technique is perturbative

in nature. This means that one can treat the system perturbatively. The dynamical Hartree-Fock approximation is certainly a good starting formalism. We are currently investigating the possibility of including higher-order correlation effects.

[18] In C_{60}, the dephasing time is long, so it does not make a significant difference on our time scale.

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[24] It is always challenging to measure the electron correlation effect both experimentally and theoretically, but decades of experimental investigations demonstrate that one is able to probe the correlation effect not only for first order but also for higher-order effects. Our results for C_{60} provide a different test case for future experiments.