Kinetic Energy-Based Normal Mode Analysis of Electronic Processes in C_{60}

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A kinetic energy-based normal-mode analysis is applied to photo-induced electronic processes in C_{60}. Due to the fact that the total kinetic energy is always a quadratic function of velocity, the expansion in normal modes is exact, in contrast to the potential-based normal-mode analysis where the total potential energy can not be exactly expanded in terms of the normal mode potentials since higher-order terms appear. This is especially true in many anharmonic relaxation processes. The calculation presented here demonstrates the appealing properties of this new scheme. In particular, the two most dominant H_g modes are identified which play an essential role in the dynamical properties of C_{60}, which is consistent with the experimental results. This clarifies the previous theoretical ambiguity which showed that the electron-phonon coupling constant is basically the same for different modes.

Key words: electronic processes in C_{60}, photoinduced excitation process, kinetic energy-based analysis.

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INTRODUCTION

Nonlinear dynamical processes are ubiquitous in physics, chemistry and biology.[1–5] The most difficult aspect is that these processes are generally highly anharmonic, for instance in fluid dynamics. Depending on different environment conditions, the dynamical process sometimes becomes rather chaotic. This challenges the existing normal-mode analysis which is based on a potential energy expansion. The reason is that the total potential energy is not equal to the summation of the total normal modes' potential energies due to the strong anharmonic nature, or in other words, the mode-mode interaction becomes stronger. This means that a brute force expansion of the total potential up to the second order,

$$V(\{\vec{r}\}) = V(\{\vec{r}_0\}) + \frac{1}{2}\sum_{i,j}\frac{\partial^2 V}{\partial r_i \partial r_j}\Delta r_i \Delta r_j + \; \dots \; , \tag{1}$$

is not sufficient. The high-order terms are not necessarily small. Moreover, the frequencies of some eigenmodes of the force matrix become imaginary. We can tentatively explain these modes as being dissipative. Clearly this statement is only meaningful in the case of weak anharmonic oscillations. However, many interesting physical phenomena, such as turbulence and ergodicity, come from precisely those anharmonic terms. This is the major deficiency of the potential energy-based normal-mode analysis. It is our belief that a reliable method treating real anharmonic dynamical processes is desirable.

In this paper, we show that these traditional difficulties can be readily overcome if one expands the total kinetic energy in terms of the normal modes. The observation is that the kinetic energy is always a quadratic function of velocity, in contrast to the potential energy expansion. This argument is quite general, irrespective of how complex the system might be. In addition, it helps to identify rather complicated properties in terms of normal modes. We will demonstrate this method for photoexcitation of C_{60}.

THEORETICAL MODEL

The model system of C_{60} consists of 60 carbon atoms situated at the vertices of 'soccer', which is described by a tight-binding Hamiltonian,[2]

$$\hat{H} = -\sum_{i>j,s} t_{i,j}\,(\hat{C}_{i,s}^{\dagger}\hat{C}_{j,s} + h.c.) + \frac{K}{2}\sum_{i,j}(\,|\,\vec{r}_i - \vec{r}_j\,| - d_0)^2, \tag{2}$$

where the first part is for the electrons with the sum running over the nearest neighbors (NN) only. Here, $t_{i,j} = t_0 - \alpha \, (|\, \vec{r_i} - \vec{r_j}\,| - d_0)$ is the NN hopping integral, where $t_0 = 1.8$ eV and $\alpha = 3.5$ eV/Å, and $\hat{C}_{i,s}^{\dagger}$ and $\hat{C}_{j,s}$ are creation and annihilation operators of the electron at atom i with spin s. The second term in the Hamiltonian is the lattice elastic energy with the summation over NN sites only, where K is the spring constant, $K = 30$ eV/Å^2, $\vec{r_i}$ is the position vector for atom i, and $d_0 = 1.54$ Å is the bond length of diamond. All parameters are chosen through fitting experimental lengths of the single and double bonds in neutral C$_{60}$ and the optical gap in solution.

For the kinetic energy-based normal-mode analysis, one also needs a reference configuration to construct the basis set for expansion. There are two ways to do this: either the initial configuration or the final relaxed configuration. For the former, in principle, we know the initial configuration and can build the basis without difficulty, but it is difficulty to know when the relaxation is complete. Of course, we can calculate the final configuration first before making the normal mode analysis. We will follow the latter scheme.

In the case of C$_{60}$, we first calculate the force matrix for the electronic and lattice parts,[5] where the dimension is 180×180. Diagonalizing this gives the eigenvectors $\vec{G_v}$. Then we expand the velocity of each atom i in terms of $\vec{G_v}$ as

$$\vec{V_i}(t) = \sum_v \mathrm{d}Q_v(t)\vec{G_v}, \tag{3}$$

where $\mathrm{d}Q_v(t)$ is the velocity of mode v at time t which can be readily calculated by the inverse transformation. It is easy to check that the total kinetic energy is equal to the summation of the kinetic energies of the normal modes. We note that in the case of the potential energy, one can not always have such equality since the high-order terms become significant. It should be pointed out that in our scheme we do not make any assumption about our dynamical process. Thus, it is a general method for nonlinear dynamics. In particular, we expect that there could be some applications in fluid dynamics.

RESULTS

The initial condition for the photoexcitation is that one electron is in the HOMO and one hole in the LUMO state. The atomic configuration is the equilibrium configuration of the unexcited C$_{60}$. In Figure 1 we schematically show the initial and final electronic structures of C$_{60}$. Due to the electron-lattice interaction, the original system now becomes unstable. In view of the

Jahn-Teller effect

$$
\begin{array}{lcr}
\text{T}_{1u} & \text{------} & \text{E}_{1u} \\
\text{(LUMO)} & & \text{A}_{2u}
\end{array}
$$

$$
\begin{array}{lcr}
\text{H}_u & \text{------} & \text{A}_{1u} \\
\text{(HOMO)} & & \text{E}_{1u} \\
& & \text{E}_{2u}
\end{array}
$$
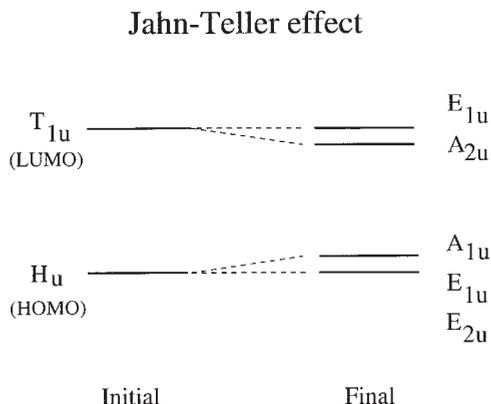
Initial   Final

Figure 1. Initial and final electronic configurations of LUMO and HOMO.

large mass of carbon atom compared with that of the electron, we follow an adiabatic approach as before,[2] where we assume the quantum fluctuations of the carbon atoms to be small. In other words, we treat the electrons quantum mechanically and the carbon atoms classically.[6] The force exerted on the carbon atoms is simply the energy derivative with respect to the positions of atoms,

$$
\vec{f_i} = - \frac{\delta E(\vec{r_i})}{\delta \vec{r_i}}, \tag{4}
$$

where E is the total energy (electron plus atom energy). In Figure 2 we plot how the total kinetic energy changes with time. We see a strong anharmonic oscillation around 0.065 eV, which reflects the complex feature of the relaxation process of photoexcitation. An examination reveals that the atoms acquire their maximum kinetic energy around 25 fs. Within this period, the electronic energy flows into the lattice. The time scale is determined by the coupling constant, the displacement of atoms and the sound velocity. After this maximum peak, the kinetic energy decays very quickly. Around 100 fs, the amplitude of the kinetic energy starts to converge. One can see that the relaxation time is about 100 fs.

Before we embark on our normal mode analysis, let us first review the normal modes of C_{60}. Since C_{60} has 180 degrees of freedom, in principle there are 180 normal modes. Since six normal modes, *i.e.*, three translational and three rotational modes, have zero frequency, in total 174 normal modes are nontrivial. C_{60} has the highest point group symmetry, and all the modes can be classified as either even or odd-parity mode. From the Jahn-Teller theorem, the relevant modes are all even-parity, while the A_g and H_g modes
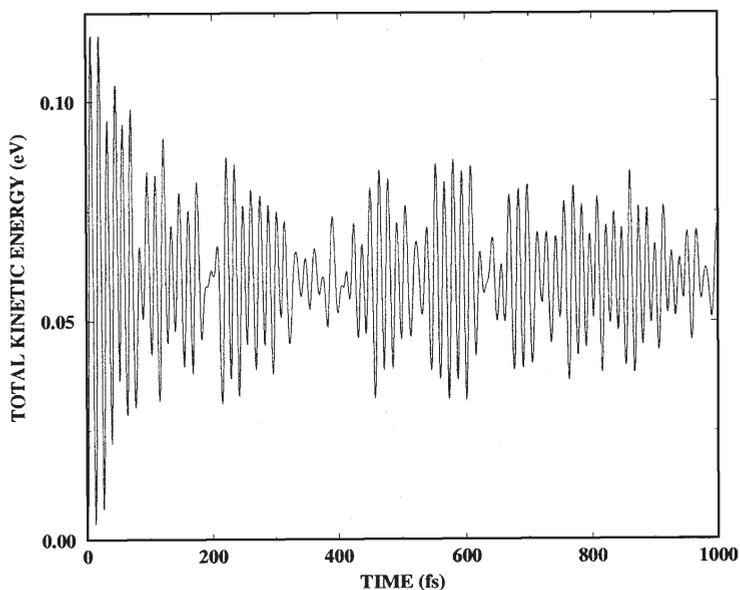
Figure 2. Time evolution of the total kinetic energy in photoexcited C$_{60}$.

are dominant during the relaxation process. However, there is a clear differ-ence between the A$_g$ and H$_g$ modes. The former behaves like the breathing mode and inhale and exhale energy periodically. They do not greatly affect the relaxation process, though they gain a sizable amount of energy. For the H$_g$ modes, by contrast, they not only absorb energy but also affect the relax-ation. This is understandable as the A$_g$ and H$_g$ modes have very different eigenvectors. In fact, the shape of the eigenvector of one dominant H$_g$ mode has an identical structure as the distorted C$_{60}$, namely, the eigenvector shows a laminar structure with maximum distortion around the equatorial area (see Figure 3). Intuitively, this mode must make a significant contribu-tion to the relaxation process, which is indeed the case.

In Figure 4 we plot the kinetic energies of the two dominant modes, H$_g$(1) and H$_g$(2), versus time. At an early stage, the H$_g$(2) mode has the larger ki-netic energy with a maximum of 0.035 eV. After 50 fs, the H$_g$(1) mode takes the lead, with its kinetic energy increasing sharply. The dominance of this mode diminishes after 100 fs. Such change regulates the distribution of ki-netic energies among these dominant modes and also indicates the comple-tion of the relaxation. We notice that the H$_g$(2) mode restores its initial dom-inance. The final stage of relaxation is largely controlled by these two modes. The important feature is that the released kinetic energy from these two dominant modes is roughly equilibrated among those other modes, each
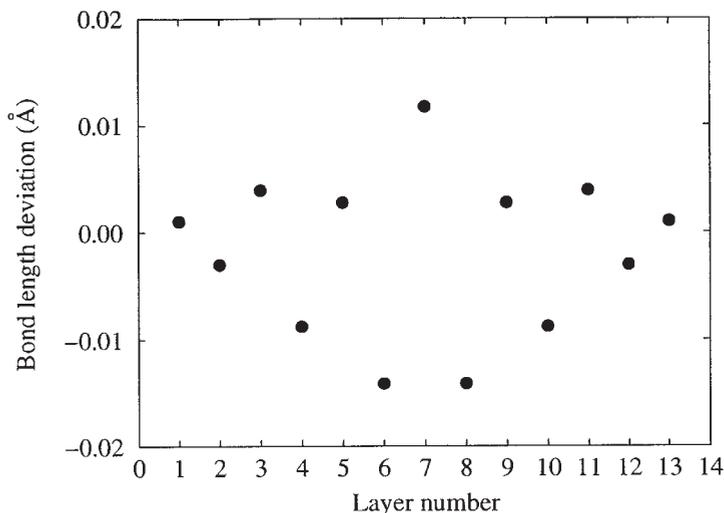
Figure 3. Framework of the normal mode $H_g(1)$ eigenvector.

of which gains a very small kinetic energy while their number is very large, which effectively forms a reservoir. In analogy to the solution, we can call these modes a heat bath since they do not contribute to the real evolution of the system. Doing so, we simplify our problem since we only need to focus on a few of the normal modes, as we did above. This is rather attractive for a problem with many degrees of freedom, which is why we expect a potential use in fluid dynamics. More interestingly, initially one could expect that totally eight normal modes will play the main role here, but from our calculation, only two of them are dominant. This means that statically eight modes are equivalent, but dynamically they are different. This piece of information is beyond the static J-T theorem and well consistent with the experimental observation.[7] Actual experiments show that the electron-phonon coupling for eight H_g modes is different, namely the constant is 0.048 for $H_g(1)$, 0.020 for $H_g(2)$ and 0.002 for $H_g(3)$. Our results do not support earlier static calculations[8] which show that the electron-phonon coupling for all the H_g modes is basically the same. The reason is that in these calculations no real dynamical effects are taken into account. The uniqueness of the normal mode analysis based on kinetic energy demonstrated here gives us some insight into the complicated relaxation mechanism of photoexcitation in C_{60}.
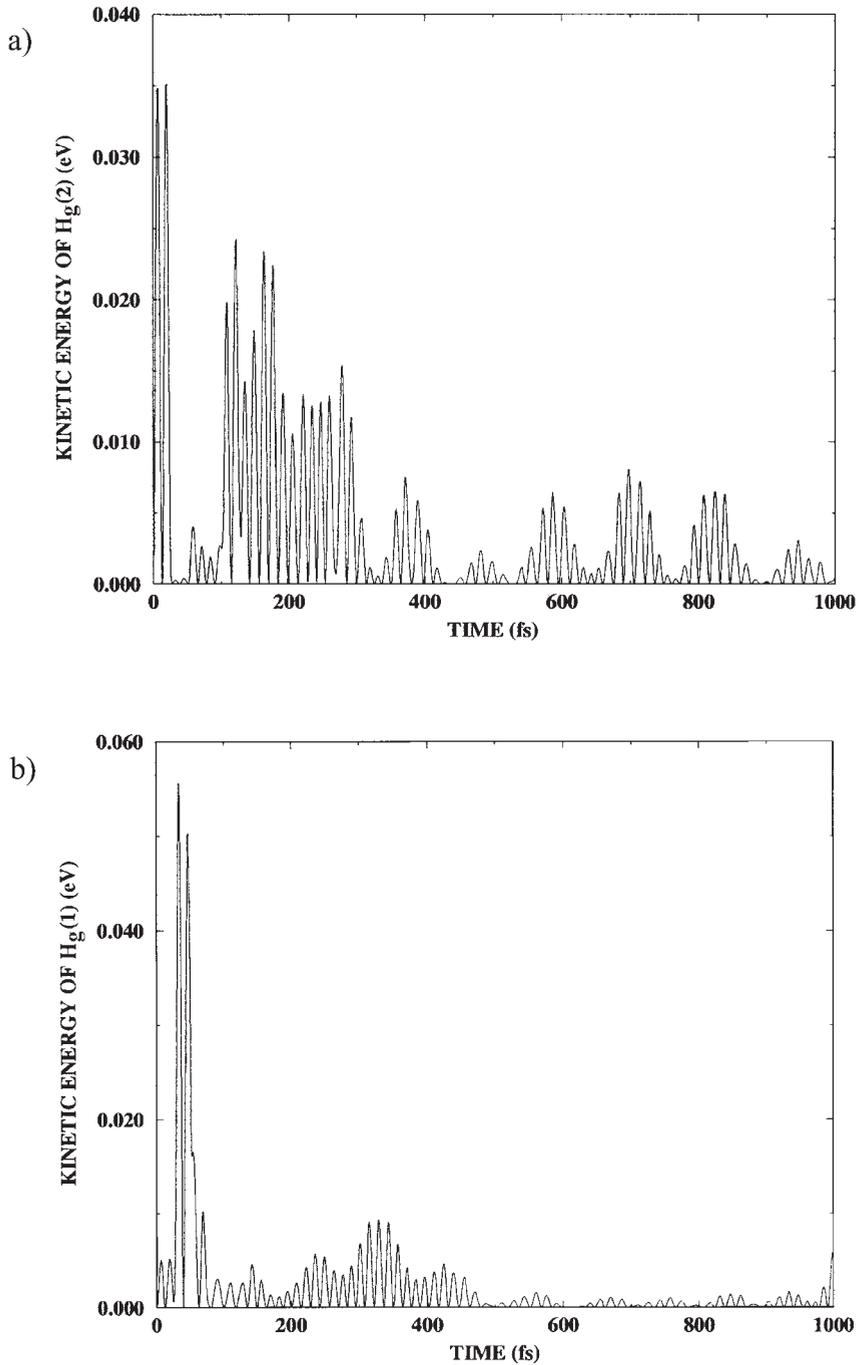
Figure 4. Kinetic energy of the two dominant modes: (a) H$_g$(2) and (b) H$_g$(1).

CONCLUSION

We have presented a kinetic energy-based normal-mode analysis of photoinduced excitation processes in C_{60}. This scheme is as simple as that based on the potential energy expansion, but it is a complete expansion of the total kinetic energy. In addition, our scheme does not depend on the complexity of the dynamical process, which is distinct from the potential energy-based expansion. The underlying reason for the success of our present scheme is that the kinetic energy is always a quadratic function of velocity. Our numerical results clearly demonstrate the appealing property of the present scheme. In particular, we find that only two modes are most relevant to the nonlinear relaxation process. Such dominance greatly simplifies our analysis, and the numerical results are well supported by the experiments, which show that for the eight H_g modes, the electron-phonon coupling constant is different, while the previous theoretical calculation predicts almost equal electron-phonon coupling constants for the different H_g modes. We argue that the major reason is the fact that the dynamical process was not properly treated in those calculations.

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6. There are several differences between the classical and quantum processes. Among the most important ones is the zero-point vibration, which is purely quantum mechanical nature and missing in the classical dynamics. Previously, we used the multiple-phonon procedure (Huang-Rhys formalism) to estimate the relaxation time, and found that the relaxation time is the same as that found for the classical simulation (for details, see G. P. Zhang, PhD. Thesis, Fudan University, Shanghai, 1995). Thus, we conclude that the CM is at least a good approximation for our purpose, as also found by others.

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SAŽETAK

Istraživanja elektronskih procesa u C$_{60}$ analizom kinetičkih energija normalnih modova

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Fotoinducirani elektronski procesi u C$_{60}$ istraženi su analizom kinetičkih energija normalnih modova. Budući da je ukupna kinetička energija uvijek kvadratna funkcija brzine, moguće je provesti egzaktan razvoj po normalnim modovima. U slučaju analize normalnih modova temeljenoj na potencijalnoj energiji, zbog pojave članova višeg reda, nije moguće ukupnu potencijalnu energiju prikazati preko doprinosa pojedinih normalnih modova, osobito za mnoge anharmonijske relaksacijske procese. Ovdje prikazani račun pokazuje privlačnost nove sheme. Identificirana su dva H$_g$ moda koji dominantno utječu na dinamička svojstva C$_{60}$, što je u skladu s eksperimentalnim rezultatima. Time je objašnjeno zašto je elektron-fononska konstanta sprege gotovo ista za različite modove.