

Lattice Relaxation Study on Self-Trapped Exciton and Biexciton in Neutral and Charged Fullerenes

Wen-Zheng Wang,¹ Chui-Lin Wang,² Zhao-Bin Su,¹ and Lu Yu^{1,3}

¹*Institute of Theoretical Physics, Academia Sinica, P.O. Box 2735, Beijing 100080, China*

²*China Center of Advanced Science and Technology (World Laboratory), P.O. Box 8730, Beijing 100080, China*

³*International Center for Theoretical Physics, P.O. Box 586, Trieste 34100, Italy*

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The formation and dynamical properties of D_{5d} -symmetry self-trapped exciton (STE) derived from the electronic $h_u \rightarrow t_{1u}$ parity-forbidden transition of neutral buckyball are studied in the presence of Coulomb interactions using the Bogoliubov-de Gennes formalism. Within the lattice relaxation theory, the multimode vibronic structures in the luminescence and absorption spectra related to STEs are elucidated in good agreement with experiments. The STEs arising from the allowed $t_{1u} \rightarrow t_{1g}$ transition of C_{60}^{1-} and C_{60}^{2-} as well as the possibility of forming a self-trapped biexciton in C_{60}^{1-} are also considered.

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Since its discovery as the third stable form of carbon [1] and a novel prototype for high-temperature superconductivity [2], the fullerene family has quickly emerged as one of the most attractive topics in physics and chemistry. Because of the weakness of the van der Waals force between molecules the electronic and vibrational properties of solid C_{60} are rather close to those of a single molecule, at least above the spinning transition temperature.

Extensive optical and magnetic resonance studies on C_{60} in solutions, matrices, and solid films [3-11] have provided very strong evidence for self-trapped excitons (STE) with the following properties: (i) For neutral C_{60} the singlet STE is derived from the dipole forbidden transition [4-7] and is mainly responsible for the photoabsorption (PA) and photoluminescence (PL). (ii) The vibronic structures have been resolved in solutions [4,5] and in solid films [6,7] which show clearly the importance of the e -ph interactions and lattice relaxation. (iii) As evidenced by the energy transfer [3], the resonance Raman and PL [8], as well as the photoluminescence detected ESR (PLDSR) and light induced ESR (LESER) studies [3,9], the lowest excited state is a triplet with a singlet-triplet splitting ~ 0.2 eV which shows the presence of e - e correlations, although not very strong. (iv) The optical and ESR measurements on anions in solutions manifest dynamical Jahn-Teller (JT) distortions in the allowed t_{1u} - t_{1g} transition [10,11]. There have been extensive the-

oretical studies on the excited states of C_{60} [12-15], but so far no detailed comparison has been made between theory and experiment, for which both the dipole forbiddenness of the transition and the lattice relaxation have to be considered.

In this Letter, we first demonstrate the existence of the STE with D_{5d} symmetry in neutral buckyballs through the solution of Bogoliubov-de Gennes (BdeG) equations with e - e interactions included. Then we elucidate the multiphonon vibronic structures associated with STE using the multimode version of the lattice relaxation theory developed by Huang and Rhys [16] and elaborated further by two of us in the context of conducting polymers [17]. This scheme successfully interprets the observed luminescence and absorption spectra. In particular, the weakness of the dipole transition relating the ground state and STE is remedied through the first-order perturbation on e -ph interactions. The optical spectra of C_{60}^{1-} and C_{60}^{2-} anions are also calculated in good agreement with experiments. Here we consider the buckyball itself and postpone all possible solid state effects for future studies.

The SSH Hamiltonian [18,19] is adopted to describe the JT active 2D buckyball [20,21]. In order to consider the optical transitions between symmetry broken states and the effect of e - e correlations of C_{60} , a SSH-like Hamiltonian can be expressed as [17] $H = H_e + H_{ph} + H_{int}$ with

$$\begin{aligned}
 H_e &= - \sum_{\langle i,j \rangle, s} t_0 (c_{i,s}^\dagger c_{j,s} + \text{H.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle i,j \rangle, s, s'} n_{i,s} n_{j, s'} + \sum_\nu \alpha (\langle b_\nu^\dagger \rangle + \langle b_\nu \rangle) F^\nu + \sum_\nu \hbar \omega_\nu \langle b_\nu^\dagger \rangle \langle b_\nu \rangle, \\
 H_{ph} &= \sum_\nu \hbar \omega_\nu [(b_\nu^\dagger - \langle b_\nu^\dagger \rangle) (b_\nu - \langle b_\nu \rangle) + \frac{1}{2}], \\
 H_{int} &= \sum_\nu (\alpha F^\nu + \hbar \omega_\nu \langle b_\nu \rangle) (b_\nu^\dagger - \langle b_\nu^\dagger \rangle) + \text{H.c.} \quad (1)
 \end{aligned}$$

where

$$F^\nu = \frac{\hbar}{\sqrt{2\hbar\omega_\nu M}} \sum_{(i,j),s} (\xi_i^\nu - \xi_j^\nu) \cdot \frac{l_1(ij)}{l_1(ij)} (c_{is}^\dagger c_{js} + \text{H.c.}) \quad (2)$$

Here α is the e -ph coupling constant, ξ_i^ν is the amplitude of normal mode ν in the homogeneous ground state [21], and $l_1(ij)/l_1(ij)$ is the unit vector along the unrenormalized bond (i, j) . b_ν^\dagger (b_ν) is the phonon creation (annihilation) operator for mode ν , while $\langle b_\nu^\dagger \rangle$, $\langle b_\nu \rangle$ are the order parameters of dynamic symmetry breaking and can be determined self-consistently within the BdeG formalism [19] through the gap equations $\hbar\omega_\nu \langle b_\nu \rangle = -\alpha \langle e | F^\nu | e \rangle$, where $|e\rangle$ is the many-electron state found from the corresponding BdeG equations. Here the unrestricted Hartree-Fock approximation has been applied to deal with the e - e interactions in H_e , which will affect the electronic and lattice structures of the ground state and the exciton formation. The set of parameters is chosen as $t_0 = 1.75$ eV, $\alpha = 4.75$ eV/Å, $U = 4.0$ eV, $V = 0.15$ eV. For the homogeneous ground state, the electronic highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap is 2.00 eV, while the difference of the bond lengths is 0.04 Å, which are compatible with the previous results [20,21]. It is noted that only the totally symmetric A_g modes can contribute to $\langle b_\nu \rangle$.

After one electron is photoexcited from HOMO to LUMO via a phonon-assisted process, the lattice instability will finally cause the whole system to relax to a stable excited state. According to our calculations using the dynamic evolution method [22], this final stable excited state is a STE with symmetry breaking from I_h to D_{5d} . The same symmetry breaking of I_h is also found for the electron-doped C_{60}^{-1} [20,21] since the perturbed electronic states are similar in these two cases. Other symmetry-breaking STEs have also been checked, but only D_{5d} STE is found to be stable. This result is consistent with the PLDMR and LESR evidences [3,9]. Since the e - e interactions have already been included in our consideration, the splitting of the spin-singlet and triplet STE can be calculated within the lowest or-

der configuration interaction approximation [23]. The self-consistently determined wave function of the singlet (triplet) STE is given as $|\Psi_\pm\rangle = \frac{1}{\sqrt{2}}(|\Psi_{\alpha\beta}\rangle \pm |\Psi_{\beta\alpha}\rangle)$, where $|\Psi_{\alpha\beta}\rangle = C_{\alpha\uparrow}^\dagger C_{\beta\downarrow}^\dagger |\mathcal{V}\rangle$, α, β denote the two relaxed singly occupied states of STE, $|\mathcal{V}\rangle$ represents the rest of the spin-doublet states. This splitting $\Delta\mathcal{E}_{s-t}$ resulting from the correlation of $|\Psi_{\alpha\beta}\rangle$ and $|\Psi_{\beta\alpha}\rangle$ turns out to be 0.20 eV. Hence, the energy of the singlet STE is determined to be 1.93 eV, while that of the triplet STE is 1.73 eV, which is compatible with the experimental observations [4,5]. The order parameters $\langle b_\nu \rangle$ are calculated for all modes, but nonvanishing values are obtained only for some Raman-active A_g modes and H_g modes. The appearance of H_g modes is due to the symmetry breaking from I_h to D_{5d} . Meanwhile, the Huang-Rhys factors [16,17], which characterize the difference of lattice relaxations for the ground state and STE, can be determined through the definition $S_\nu = (\langle b_\nu \rangle_{\text{STE}} - \langle b_\nu \rangle_g)^2$. Only five S_ν corresponding to the pentagon pinch A_g mode and $H_g(1)$, $H_g(4)$, $H_g(7)$, and $H_g(8)$ modes (experimentally 273, 774, 1428, and 1575 cm^{-1}) do not vanish, with values 0.24, 1.53, 0.24, 0.13, and 0.55, respectively.

The pure electronic transition from HOMO to LUMO is parity forbidden, so the observed subgap vibronic structures are attributed to the phonon-assisted STE, and this vibronic transition is assigned to the singlet sector of the lowest STE [5,6]. However, the electronic dipole moment related to the transition from the ground state 1A_g to the lowest singlet STE $^1T_{2g}$ is unfortunately very small compared with the first parity-allowed transition $^1T_{1u}$, because the lattice relaxation leading to D_{5d} STE is still not enough to break the parity of the electronic states effectively, as illustrated by the small values of the Huang-Rhys factors for the relaxed modes. Thus the optical intensities from higher electronic states should be lent to trigger the actual transition with the assistance of the corresponding phonon process [24]. Using the first order perturbation of e -ph interactions H_{int} , the dipole moment of this transition can be given in the low temperature limit (i.e., $n_i^0 = 0$) as

$$\begin{aligned} \langle e_f n_f | \hat{r} | e_i n_i \rangle &= \sum_{s(\neq i)} \frac{\langle e_s^0 n_s^0 | H_{\text{int}} | e_i^0 n_i^0 \rangle}{\mathcal{E}_s^0 - \mathcal{E}_i^0} \langle e_f | \hat{r} | e_s^0 \rangle \langle n_f^0 | n_s^0 \rangle + \sum_{t(\neq i)} \frac{\langle e_f^0 n_f^0 | H_{\text{int}} | e_t^0 n_t^0 \rangle}{\mathcal{E}_f^0 - \mathcal{E}_t^0} \langle e_t^0 | \hat{r} | e_i^0 \rangle \langle n_t^0 | n_i^0 \rangle \\ &= \sum_l \left[M_{fi}^l \langle n_f^{0l} | 1 \rangle + M_{fi}^{l+} \sqrt{n_f^{0l}} \langle (n_f^{0l} - 1) | 0 \rangle + M_{fi}^{l-} \sqrt{n_f^{0l} + 1} \langle (n_f^{0l} + 1) | 0 \rangle \right] \prod_{l' \neq l} \langle n_f^{0l'} | 0 \rangle, \quad (3) \end{aligned}$$

where

$$\begin{aligned} M_{fi}^l &= \sum_{s(\neq i)} \frac{\langle e_s^0 | \alpha F^l | e_i^0 \rangle}{\mathcal{E}_s^0 - \mathcal{E}_i^0 + \hbar\omega_l} \langle e_f | \hat{r} | e_s^0 \rangle, \\ M_{fi}^{l\pm} &= \sum_{t(\neq f)} \frac{\langle e_f^0 | \alpha F^l | e_t^0 \rangle}{\mathcal{E}_f^0 - \mathcal{E}_t^0 \pm \hbar\omega_l} \langle e_t^0 | \hat{r} | e_i^0 \rangle. \quad (4) \end{aligned}$$

Here \mathcal{E}_s^0 , \mathcal{E}_i^0 are the unperturbed electronic energies of the

states $|e_s^0\rangle$ and $|e_i^0\rangle$, while the total energy difference is $\mathcal{E}_s^0 - \mathcal{E}_i^0 = \epsilon_s^0 - \epsilon_i^0 + \sum_l \hbar\omega_l n_s^l$. The unperturbed intermediate states $|e_s^0 n_s^0\rangle$ and $|e_t^0 n_t^0\rangle$ are defined with respect to the corresponding phonon vacua of $|e_i^0 n_i^0\rangle$ and $|e_f^0 n_f^0\rangle$, so only a single-phonon process can take place. Thus the optical spectral function of this phonon-assisted transition in the low temperature limit is derived as

$$\begin{aligned}
I(\hbar\omega) = & \sum_{\{n_f^{0\mu}\}} \left| \sum_{\mu} [M_{fi}^{\mu} \langle n_f^{0\mu} | 1 \rangle + M_{fi}^{\mu+} \sqrt{n_f^{0\mu}} \langle (n_f^{0\mu} - 1) | 0 \rangle \right. \\
& + M_{fi}^{\mu-} \sqrt{n_f^{0\mu} + 1} \langle (n_f^{0\mu} + 1) | 0 \rangle] \prod_{\mu' (\neq \mu)} \langle n_f^{0\mu'} | 0 \rangle \left. \right|^2 \delta \left(\hbar\omega - \mathcal{E}_{\text{STE}} \mp \sum_{\mu} n_f^{0\mu} \hbar\omega_{\mu} \right) \\
& + \sum_{\{n_f^{0\mu}\}} \sum_{\nu} \left| M_{fi}^{\nu} + M_{fi}^{\nu+} \right|^2 \prod_{\mu} \left| \langle n_f^{0\mu} | 0 \rangle \right|^2 \delta \left(\hbar\omega - \mathcal{E}_{\text{STE}} \mp \sum_{\mu} n_f^{0\mu} \hbar\omega_{\mu} \mp \hbar\omega_{\nu} \right). \quad (5)
\end{aligned}$$

where \mp corresponds to absorption or emission, respectively, μ, μ' denote modes with nonvanishing Huang-Rhys factors, while ν denotes other unrelaxed modes. $\langle n_f^{\mu} | 1 \rangle$ and $\langle n_f^{\mu} | 0 \rangle$ are the Franck-Condon overlap integrals related to the Huang-Rhys factors S_{μ} [16] via $\langle n_f^{\mu} | n_i^{\mu} \rangle = e^{-\frac{S_{\mu}}{2}} \left(\frac{n_i^{\mu}!}{n_f^{\mu}!} \right)^{\frac{1}{2}} (-S_{\mu})^{\frac{n_i^{\mu} - n_f^{\mu}}{2}} L_{n_i^{\mu} - n_f^{\mu}}^{n_i^{\mu}}(S_{\mu})$, where $L_n^m(z)$ is the associated Laguerre polynomial.

The calculated luminescence and absorption spectra driven by the singlet STE are shown in Fig. 1, where the experimental observed lines (with height proportional to the relative intensity) of Refs. [4] and [5] are also marked. The contribution from the first term of Eq. (5) to the optical intensity represents the exciton effect by itself, which is about 2 orders of magnitude smaller than the second term representing the effect of linear vibronic coupling. For luminescence, the one-phonon Stokes shifts mainly originate from IR-active $T_{1u}(4)$ (experimentally 1429 cm^{-1}) and $H_u(1)$, $H_u(4)$, and $H_u(7)$ modes, while for absorption, the peaks arising from the one-phonon shifts are mainly due to $T_{1u}(3)$, $T_{1u}(4)$ and $H_u(1)$, $H_u(4)$, $H_u(7)$ modes. The calculated vibronic structures due to replicas belonging to buckyball pinch mode, and the four JT active H_g modes, agree very well (for both the positions and the relative intensities) with the observations by Wang for luminescence [5] and by Whetten *et al.* for absorption [4]. The obtained intensities for luminescence and absorption are lower by about 2 orders of magnitude than that of parity-allowed ${}^1T_{1u}$ transition which is also consistent with observations. The main deviations from the experiments are due to inaccuracy of the calculated phonon spectra and using their values in the ground state to calculate both absorption and emission. Thus the results are expected to fit the luminescence better than the absorption experiments. In view of the simplicity of the model itself, the agreement on the peak positions and relative intensities is very satisfactory. On the other hand, the present result, which is applicable to the gas or solution spectrum (since only a single buckyball is considered), cannot be directly applied to explain the difference between the experiments in solutions and solids. The symmetry properties of the single buckyball would be modified by the solid-state effects.

Now consider the charged fullerenes. The dynamic evolution method is also employed to obtain the STE solutions within the BdeG formalism. The optimized station-

ary configurations of the ground state C_{60}^{1-} and C_{60}^{2-} molecules also possess D_{5d} symmetry [20,21], while those of the STE states derived from the electronically allowed transition $t_{1u} \rightarrow t_{1g}$ are determined to be of D_{2h} and C_{2h} symmetries, respectively. Taking into account the fact that there are six equivalent D_{5d} STE configurations and fifteen degenerate D_{2h} and C_{2h} STE configurations, the absorption spectra are obtained without involving additional single-phonon process, as plotted in Fig. 2. It is noted that unlike the neutral C_{60} the phonon replica in this figure arise from the four JT active H_g modes without contribution of the A_g mode, and the mirror symmetry should be applied to obtain the corresponding emission spectra for this allowed transition. This calculated spectrum for C_{60}^{1-} is compatible with the observations by Kato *et al.* [11]. The 0.11 eV blueshift of the 0-0 peak in C_{60}^{2-} with respect to that in C_{60}^{1-} mainly results from the calculated singlet-triplet splitting 0.17 eV present in C_{60}^{2-} . This shift is compatible with the observed value 0.16 eV [25]. Compared with the experimental result [11], our absolute value for STE energy is shifted by 0.5 eV, which we believe is due to the mean field nature of the BdeG formalism. Interestingly, the STBE of C_{60}^{1-} derived from the electronically allowed $t_{1u} \rightarrow t_{1g}$ and $h_u \rightarrow t_{1g}$ processes can be obtained with the resulting C_{2h} distortions and 0.082 eV binding energy. The STBE could be detected in the two-photon

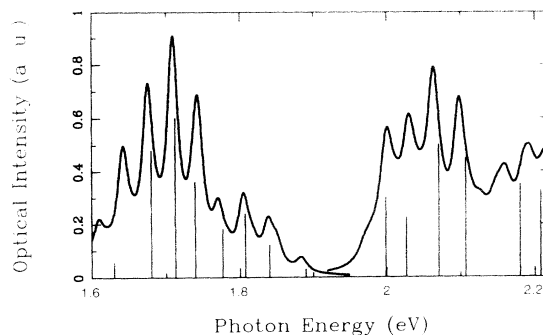


FIG. 1. The calculated luminescence and absorption spectra due to STE at $T \sim 0 \text{ K}$. The vertical bars (with height proportional to the intensity) indicate the experimental results of Refs. [4,5], while the Lorentzian broadening is 0.01 eV.

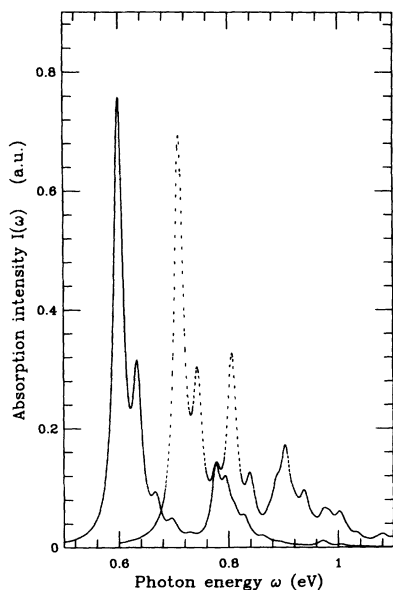


FIG. 2. The calculated absorption spectrum for charged C_{60} . The solid line represents the result for C_{60}^{1-} , while the dotted line is for C_{60}^{2-} . The Lorentzian broadening is 0.01 eV.

measurements as in the case of semiconductors [26].

In summary, we have shown that the lattice relaxation approach adopted here allows us to interpret almost quantitatively the experimentally observed optical absorption and PL spectra for the buckyball. The set of parameters in the model (t_0 , α , U , and V) have commonly used values and are consistent with the observed gap. All the rest comes from the calculation itself, without any further adjustable parameters. Thus the BdeG formalism combined with the lattice relaxation approach is very successful in describing the dynamical symmetry breaking of the ground and excited states of the fullerenes.

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