Modeling of Electrons and Excitons Multiple-Exciton-Generation Dynamics in Silicon Clusters using Many-body Green’s Function Theory

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The electrons and excitons multiple-exciton-generation dynamics in two silicon clusters, or more specifically the inelastic scattering rates of electronic and excitonic states in the two silicon clusters, Si26 and Si46, are calculated using many-body Green’s function theory. The nonradiative relaxation rates of these states are calculated by the Fermi’s golden rule as well. The multiple exciton generation (MEG) features of electronic and excitonic excitations are investigated by direct comparison of inelastic scattering and nonradiative relaxation rates. The effects of cluster size, excitation energy and temperature on the MEG performance of the electronic and excitonic excitations in the two silicon clusters simulated are analyzed. For electronic excitations, it is found that the larger cluster is more suitable for the MEG application, since it can cover a broader energy range with lower MEG energy-threshold. For excitonic excitations, the nonradiative relaxation process is fast in all cases, and thus the concept of the absolute phonon bottleneck does not apply. Yet, the smaller cluster exhibits better excitonic MEG performance, indicating that the relative phonon bottleneck still holds. The remarkable differences between the MEG characteristics of the electronic states and the excitonic states are analyzed as well, and are attributed to the different exponential factors of the densities of states, which are linear and quadratic to the number of valance electrons for electrons and excitons, respectively.

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I. INTRODUCTION

The spontaneous relaxation of electronic and excitonic states with high excitation energies in semiconductor nanoclusters (SCNCs) is fundamentally important since it determines the basic electronic and optical properties of SCNCs such as photovoltaics, light-emitting diodes and lasers.\textsuperscript{1,2} The decay of electronic or excitonic states in SCNCs is a complicated dynamic process involving several different relaxation mechanisms, and two of the most important and interesting ones are the inelastic scattering process and the non-radiative relaxation process. In the inelastic scattering process, an electronic (excitonic) state transits to low-energy states and transfer its extra energy to another electron, which is promoted from the valence band to the conduction band during the interaction. In the non-radiative relaxation process (also known as phonon-assisted relaxation), an electronic (excitonic) state couples with lower energy levels, and converts the extra energy into the vibrational energy of the nuclei.

A process that involves both the inelastic scattering process and the non-radiative relaxation process is the multiple exciton generation (MEG) process in SCNCs, a fundamental process with wide potential applications such as the efficiency enhancement of single-junction photovoltaic devices.\textsuperscript{3} The mechanism of MEG is that an initial energetic state created by the incident photon could generate an extra exciton via the inelastic scattering process (also known as the impact ionization process) and increases the photocurrent of the photovoltaic devices.\textsuperscript{4} The inelastic scattering rate basically represents the rate of the MEG process. A counterpart process is non-radiative relaxation process, where the phonon-assisted relaxation occurs swiftly, and competes with the MEG process and thus deteriorating the MEG performance. It must be pointed out that the quantum confinement effect in SCNCs discretizes continuous energy bands, and produces mismatch between the electronic energy states and phonon energies. This effect may significantly slow down the non-radiative relaxation, and generate phonon bottleneck.

Experimental investigations for MEG effects in different SCNCs have been reported,\textsuperscript{5,6} yet there is still a controversy for the relation between the spatial confinement and the enhancement of MEG efficiency.\textsuperscript{7,8} The controversy mostly arises from the fact that both the inelastic scattering process and nonradiative relaxation process are size-dependent and manifest themselves in experimental data, which makes it extremely difficult to establish the relation between the sizes of SCNCs and MEG efficiencies solely based on these experimental data. Physics-based (first-principal) computations for both processes are badly needed for understanding the processes and for elucidating the experimental results.

The inelastic scattering rates of electrons and excitons in materials can be properly calculated within the framework of the many-body Green’s-function theory (MBGFT). The MBGFT-based GW method has been proven to be an accurate approach for the investigation of energies of electrons, or more precisely, quasiparticles (QPs) including quasielectrons and quasiholes, in a vast range of materials.\textsuperscript{9-11} By reserving the non-local and frequency-dependent terms of the electronic self-energy operator, the GW method is capable to capture the dynamic features of electrons in a
many-body system, such as electronic inelastic scattering rates. The method has been applied to the simulations of electronic inelastic scattering lifetimes in bulk materials, and in isolated clusters.

The computation for excitonic properties is more complicated, since an exciton state only can be correctly described by the Bethe-Salpeter equation (BSE), which explicitly includes the screened interaction between the electron and the hole. While the excitonic energies in bulk materials and in molecules can be obtained by solving the static BSE (SBSE), which is relatively easy to implement with all frequency-dependent features removed, the excitonic inelastic scattering rates, in principle, can only be calculated by solving the dynamic BSE (DBSE) with all frequency-dependent terms reserved. This presents a daunting numerical challenge, considering that the whole interaction kernel matrix needs to be updated for each excitonic state in computational implementation. An approximation approach has been proposed for the estimation of the excitonic inelastic scattering rates based on the GW electronic inelastic scattering rates and particle-hole amplitudes obtained by the time-dependent local density approximation (TDLDA). With this approximation it is possible to calculate the excitonic inelastic scattering rates in SCNCs with moderate computational expense.

The phonon-assisted relaxation of electronic and excitonic states in molecules and clusters has been investigated in terms of the transitions among different adiabatic states. In this picture, the transition rates can be evaluated based on the Fermi’s golden rule, with the non-adiabatic coupling terms as the perturbation Hamiltonian. In most researches the electronic states and excitonic states are not well distinguished, and the relaxation processes of the two types of excitation states are treated without distinction, namely within the one-particle picture. This approach works for electrons and holes that are essentially one-particle states. Treating excitons in the framework of one-particle implies the independent-transition approximation, where each transition only occurs between two one-particle states, with one in the valence band (hole) and the other in the conduction band (electron). With this approximation the decay of an excitonic state can be simplified as the decay of its electron component or its hole component. The approach approximately works for the first several excitonic states, while in general it breaks down for excitons with high excitation energies. As will be shown in this paper, the two-particle (exciton) space can be regarded as the direct product of two one-particle (electron and hole) spaces, and thus has much more dense density of states, which eventually leads to high nonradiative relaxation rates.

In this paper, the MEG features of two silicon clusters Si26 and Si46 are investigated. The electronic and excitonic states are strictly distinguished. Inelastic scattering rates of electrons are calculated with the GW method, which are further used to estimate the inelastic scattering rates of excitons. Nonradiative relaxation rates of electrons and excitons are simulated in the framework of one-particle and two-particle approach, respectively. The size and energy effects on the rates of the inelastic scattering process and nonradiative relaxation process of electronic and excitonic states are presented and analyzed. The temperature effect on the MEG performance of the silicon clusters studied is presented as well.
II. METHODOLOGY

A. Many-Body Green’s Function Theory

The electronic energies of a many-body system can be obtained by solving the quasiparticle (QP) equation

\[
(T + V_{\text{ext}} + V_H) \phi_i (r) + \int d r' \Sigma_{xc} (r, r'; E_i) \phi_i (r') = E_i \phi_i (r)
\]  

(1)

where \( T \) is the kinetic energy operator, \( V_{\text{ext}} \) the external potential, \( V_H \) the Hartree potential, \( E_i \) and \( \phi_i \) the energy and wavefunction of the \( i \)th QP, and \( \Sigma_{xc} (r, r'; E_i) \) the exchange-correlation self-energy operator. The QP equation is solved based on the results of the density functional theory (DFT)

\[
(T + V_{\text{ext}} + V_H) \phi_i (r) + V_{xc} (r) \phi_i (r) = E_i \phi_i (r)
\]

(2)

where \( E_i \) and \( \phi_i \) are the eigenvalue and eigenfunction of the \( i \)th Kohn-Sham (KS) particle respectively, and \( V_{xc} (r) \) the exchange-correlation potential. With the assumption that the KS eigenfunctions agree well with the QP wavefunctions in most cases,\(^1\) QP energies are usually solved with perturbative method to the first order

\[
\left( \phi_i \right| \Sigma_{xc} (r, r'; E_i) \left| \phi_i \right> - \left( \phi_i \right| V_{xc} (r) \left| \phi_i \right> = E_i - E_i,
\]

(3)

According to Hedin’s equations,\(^9\) \( \Sigma_{xc} = i \hbar G W \Gamma \), where \( \Gamma \) is the vertex function and \( G \) is the one-particle Green’s function

\[
G(r, r'; E) = \sum_n \frac{\phi_n (r) \phi_n (r')}{{E - E_n + i\eta_n}^{0^+}}.
\]

(4)

The coefficient \( \eta_n \) is +1 for unoccupied states and -1 for occupied states. \( W \) is the screened Coulomb interaction which can be written as

\[
W = V + V \Pi V,
\]

(5)

where \( V (r, r') \) is the Coulomb interaction, and \( \Pi (r, r'; E) \) is the reducible polarizability and can be expressed as the summation of well-defined resonant modes.\(^1\)

\[
\Pi (r, r'; E) = 2 \sum_s \left[ \frac{\rho_s (r) \rho_s (r')}{E - (\nu_i - i0^+)} - \frac{\rho_s (r) \rho_s (r')}{E + (\nu_i - i0^+)} \right]
\]

(6)

where
\begin{equation}
\rho_i(r) = \sum_{\nu, \epsilon} R_{\nu, \epsilon}^i \phi_i^* (r) \phi_{\nu, \epsilon} (r)
\end{equation}

The energies \( \nu_i \) and amplitudes \( \rho_i(r) \) of the reducible polarizability \( \Pi \) are determined by time-dependent adiabatic local density approximation (TDLDA).

The imaginary parts of the QP energies can be obtained by applying analytical continuation of \( \Sigma_{\omega} (r, r'; E) \) in the complex energy plane, and the complex QP energy \( E_i - i \eta \gamma_i^{-e} \) is calculated by solving a complex equation set numerically

\begin{align}
\text{Re} \left\{ \phi_i \left[ \Sigma_{\omega} \left( E_i - i \eta \gamma_i^{-e} \right) \right] \phi_i \right\} - \langle \phi_i | V_{\omega uv} | \phi_i \rangle &= E_i - \epsilon_i \quad \text{(8a)} \\
\text{Im} \left\{ \phi_i \left[ \Sigma_{\omega} \left( E_i - i \eta \gamma_i^{-e} \right) \right] \phi_i \right\} &= \gamma_i^{-e} \quad \text{(8b)}
\end{align}

where \( \gamma_i^{-e} \) is the inelastic scattering rate of the \( i \)th QP, and the superscript ‘e-e’ stands for electron-electron interaction.

An excitonic state of a system with \( N \) electrons essentially involves two particles, which can be investigated by the Bethe-Salpeter equation (BSE)\(^2\)\(^{20,21}\)

\begin{equation}
L(1,2;1',2') = G(1,2')G(2,1') + \int d(33'44')G(1,3)G(3',1') \Xi(3,4';3',4)L(4,2;4',2'), \quad (9)
\end{equation}

where \( L(1,2;1',2') \) is the two-particle correlation function. In Eq. (9) a integer label is assigned to a set of space, spin and time variables, namely \( (1) = (x_1, t_1) = (r_1, \sigma_1, t_1) \).

The integral kernel \( \Xi \) can be approximated as

\begin{equation}
\Xi(3,4';3',4) = -i \delta(3,3') \delta(4^+,3') V(3,4) + i \delta(3,4) \delta(3',4') W(3^+,3') \quad (10)
\end{equation}

Thus the BSE Eq. (8) can be converted to a complex eigenvalue problem\(^2\)\(^{22,14}\)

\begin{equation}
\left[ \left( E_i - i \gamma_i^{-e} \right) - \left( E_v + i \gamma_v^{-e} \right) \right] A'_{\nu, \epsilon} + \sum_{\nu', \epsilon'} A'_{\nu', \epsilon'} \left( K_{\nu' \epsilon'; \nu, \epsilon} + K_{\nu \epsilon; \nu', \epsilon'} \right) = \left( \Omega_{\nu} - i \Gamma_{\nu}^{-e} \right) A'_{\nu, \epsilon} \quad (11)
\end{equation}

where the complex eigenvalue \( \Omega_{\nu} - i \Gamma_{\nu}^{-e} \) represents the excitation energy \( \Omega_{\nu} \) and the inelastic scattering rate \( \Gamma_{\nu}^{-e} \) of the \( \nu \)th exciton. In this paper, only singlet excitations are considered, and thus the exchange term \( K_{\nu \epsilon; \nu' \epsilon'}^{x} = 2 \langle \phi_{\nu, \epsilon} | V | \phi_{\nu' \epsilon'} \rangle \). The direct interaction term \( K_{\nu \epsilon; \nu' \epsilon'}^{d} \) can be calculated as
Actually Eq. (11) explicitly includes four terms related to the decay of the exciton, which are illustrated by the Feynman diagrams in FIG.1.

FIG. 1. Feynman diagrams of terms in Eq. (11) related to the decay of particle-hole excitations. Arrowed lines are Green’s functions. Wiggled lines are screened interactions. Diagrams A and B correspond to the diagonal elements in Eq. (14). Diagrams C and D denote the screened particle-hole interaction in Eq. (12).

However, it is unfeasible to solve the DBSE Eq. (11) directly, since the matrix on the left hand side is explicitly dependent on the eigenvalues \( \Omega \) to be solved. We have demonstrated that an approximate method that only takes into account the first two diagrams in Fig. 1 can be used to estimate the excitonic decay rates \( \Gamma_{\epsilon^-\epsilon} \) as

\[
\Gamma_{\epsilon^-\epsilon} = \sum_{\nu,\nu'} |R_{\nu\nu'}|^{2} (\gamma_\epsilon + \gamma_{\epsilon'})
\]

(13)

The results obtained by the approximation approach are found to be in good agreement with those obtained by the DBSE in the case of Si20 cluster. Therefore in this paper, all excitonic decay rates are calculated by Eq. (estimate), instead of the time-consuming DBSE.

**B. Electron-Vibration Interaction**

The Hamiltonian of a system composed of electrons and nuclei can be expressed as

\[
H = T(r) + T(Q) + U(r,Q),
\]

(14)
where \( \mathbf{r} \) and \( \mathbf{Q} \) are coordinates of electrons and nuclei respectively, \( T(\mathbf{r}) \) and \( T(\mathbf{Q}) \) the kinetic energy operators of electrons and nuclei, \( U(\mathbf{r}, \mathbf{Q}) \) the total potential energy among all electrons and nuclei.

Within the Born-Oppenheimer approximation, the wavefunctions of electrons and nuclei are assumed to be independent. Thus the wavefunctions \( \Phi_i(\mathbf{r}, \mathbf{Q}) \) and energies \( E_i(\mathbf{Q}) \) of electrons can be obtained for each nuclear configuration \( \mathbf{Q} \) by solving the electronic Schrodinger equation

\[
\left[ T(\mathbf{r}) + U(\mathbf{r}, \mathbf{Q}) \right] \Phi_i(\mathbf{r}, \mathbf{Q}) = E_i(\mathbf{Q}) \Phi_i(\mathbf{r}, \mathbf{Q}) .
\]  

(15)

The wavefunction \( \psi(\mathbf{r}, \mathbf{Q}) \) of the whole system can be expanded with \( \Phi_i(\mathbf{r}, \mathbf{Q}) \) as the basis

\[
\psi(\mathbf{r}, \mathbf{Q}) = \sum_i \chi_i(\mathbf{Q}) \Phi_i(\mathbf{r}, \mathbf{Q}).
\]  

(16)

Substituting this wavefunction into the Schrodinger equation of the system, one has

\[
H \psi(\mathbf{r}, \mathbf{Q}) = \left[ T(\mathbf{r}) + T(\mathbf{Q}) + U(\mathbf{r}, \mathbf{Q}) \right] \psi(\mathbf{r}, \mathbf{Q}) = V \psi(\mathbf{r}, \mathbf{Q}),
\]  

(17)

then projecting both sides to the electronic wavefunction \( \Phi_j(\mathbf{q}, \mathbf{Q}) \), one obtains a set of coupled equations for \( \chi_i(\mathbf{Q}) \)

\[
\sum_i H_{ij}(\mathbf{Q}) \chi_i(\mathbf{Q}) = V \chi_j(\mathbf{Q})
\]  

(18)

where \( V \) is the energy of the state \( \psi(q, \mathbf{Q}) \), and \( H_{ij}(\mathbf{Q}) \) is

\[
H_{ij}(\mathbf{Q}) = H_{ij}^0(\mathbf{Q}) + H_{ij}^1(\mathbf{Q})
\]  

(19)

\[
H_{ij}^0(\mathbf{Q}) = \delta_{ij} \left[ E_i(\mathbf{Q}) - \sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} \right]
\]  

(20)

\[
H_{ij}^1(\mathbf{Q}) = -\sum_k \frac{\hbar^2}{2M_k} \left( 2 \left< \Phi_j \left| \frac{\partial}{\partial Q_k} \right| \Phi_i \right> \frac{\partial}{\partial Q_k} + \left< \Phi_j \left| \frac{\partial^2}{\partial Q_k^2} \right| \Phi_i \right> \right)
\]  

(21)

where \( M_k \) are the masses of the normal coordinates \( Q_k \).

Within the adiabatic approximation, non-adiabatic coupling term \( H_{ij}^1(\mathbf{Q}) \) is neglected. Therefore the Hamiltonian matrix becomes diagonal, and Eq. (18) is simplified as
\[
\left( E_i(Q) - \sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} \right) \chi_i(Q) = V \chi_i(Q) \tag{22}
\]

which implies the nuclei move on the adiabatic potential energy surface (PES) \( E_i(Q) \). The nuclear wavefunctions \( \chi_i(Q) \) can be obtained by solving Eq. (22).

Within the harmonic approximation, all anharmonic effects are neglected. Thus \( E_i(Q) \) can be expressed as the linear combination of linear and quadratic terms,

\[
E_i(Q) = \sum_k \alpha_k Q_k^2 + \sum_k \beta_k Q_k + \sum_{k,l} \gamma_{k,l} Q_k Q_l \tag{23}
\]

where \( \alpha_k, \beta_k, \gamma_{k,l} \) are coefficients. By choosing the equilibrium position as the origin \( Q_0 \), \( \alpha_k \) can be eliminated. For normal coordinates \( Q_k \), bilinear terms vanish and \( \gamma_{k,l} = 0 \). Therefore Eq. (22) yields \( k \) independent one-dimensional harmonic-oscillator equations which have analytical solutions \( \theta_{k,v_i}(Q_k) \) with \( v_k \) the quantum numbers. Then the nuclear wavefunction \( \chi_{i,v}(Q) \) is expressed as

\[
\chi_{i,v}(Q) = \prod_Q \theta_{i,v_i}(Q_i), \tag{24}
\]

where \( v = (v_1, v_2, \ldots, v_k) \).

Within the perturbation approximation, the nonradiative transition rate between any two adiabatic states \( \chi_{i,v'}(Q)\Phi_i(r,Q) \) and \( \chi_{j,v''}(Q)\Phi_j(r,Q) \) with energies \( V_{i,v'} \) and \( V_{j,v''} \) can be calculated with the Fermi’s golden rule by taking \( H_{ij}(Q) \) as the perturbation Hamiltonian,\(^{23}\)

\[
W_{i\rightarrow j} = \frac{2\pi}{\hbar} \sum_{v',v''} P_{v'} \left| \left< \chi_{j,v''} \right| H_{ij} \left| \chi_{i,v'} \right> \right|^2 \delta \left( V_{j,v''} - V_{i,v'} \right) \tag{25}
\]

where the summation is over all initial vibronic states \( v' \) weighted by the Boltzmann factor \( P_{v'} \), and all final vibrational states \( v'' \). The perturbation term is

\[
\left< \chi_{j,v''} \right| H_{ij} \left| \chi_{i,v'} \right> = -\sum_k \frac{\hbar^2}{2M_k} \left< \Phi_j \chi_{j,v''} \left| \frac{\partial \Phi_i}{\partial Q_k} \frac{\partial \chi_{i,v'}}{\partial Q_k} \right> \right> - \sum_k \frac{\hbar^2}{2M_k} \left< \Phi_j \chi_{j,v''} \left| \frac{\partial \Phi_i}{\partial Q_k} \frac{\partial \chi_{i,v'}}{\partial Q_k} \right> \right> \tag{26}
\]

The second term in Eq (26) are usually neglected with the assumption that electronic wavefunctions are slowly varying functions of normal coordinates \( Q_k \), and Eq (26)
becomes\(^{24-26}\)

\[
\langle \chi_{j}, \omega' | H_0 | \chi_{i}, \omega'' \rangle = -\sum_k \frac{\hbar^2}{M_k} \left( \Phi_j \hat{\partial} \Phi_i \right) \langle \chi_{j}, \omega' | \chi_{i}, \omega'' \rangle
\]  

(27)

Within the displaced potential surface (DPS) approximation, the normal coordinates \(Q_k\) and their masses \(M_k\) and frequencies \(\omega_k\) are assumed to be constant for all electronic and excitonic states. Only the equilibrium positions \(Q_k^0\) change for different states, namely \(Q_k^{0,i} \neq Q_k^{0,j}\). Define the dimensionless displacements \(\Delta_{k}^{i,j}\) as

\[
\Delta_{k}^{i,j} = \left( \frac{M_k \omega_k}{\hbar} \right)^{1/2} (Q_k^{0,i} - Q_k^{0,j}).
\]  

(28)

The energy associated with the potential surface displacement between electronic states \(\Phi_i\) and \(\Phi_j\) is

\[
E_{M}^{i,j} = \frac{1}{2} \sum_k \hbar \omega_k \left( \Delta_{k}^{i,j} \right)^2
\]  

(29)

In the strong coupling case, the nonradiative transition rate Eq (25) becomes\(^{26-28}\)

\[
W_{i\rightarrow j} = \sum_k \left( \frac{\Phi_j \hat{\partial} Q_i | \Phi_i}{\hbar \omega_k (2\pi)^{1/2}} \right) \frac{\hbar \omega_k (2\pi)^{1/2}}{2M_k D_{i,j}} \left( I_{k}^{i,j} + I_{k}^{j,i} \right)
\]  

(30)

where

\[
D_{i,j} = \frac{1}{2} \sum_k \omega_k^2 \left( \Delta_{k}^{i,j} \right)^2 (2\bar{n}_k + 1)
\]  

(31)

\[
\bar{n}_k = \frac{1}{\exp \left( \hbar \omega_k / k_B T \right) - 1}
\]  

(32)

\[
I_{k}^{i,j} = \left( \coth \frac{\hbar \omega_k}{2k_B T} + 1 \right) \exp \left( - \frac{\Delta E_{i,j} - \hbar \omega_k - E_{M}^{i,j}}{2D_{i,j} \hbar^2} \right)
\]  

(33)

\[
I_{k}^{j,i} = \left( \coth \frac{\hbar \omega_k}{2k_B T} - 1 \right) \exp \left( - \frac{\Delta E_{i,j} + \hbar \omega_k - E_{M}^{i,j}}{2D_{i,j} \hbar^2} \right)
\]  

(34)

\[
\Delta E_{i,j} = E_{0,j} - E_{0,i}
\]  

(35)

Note that \(E_{0,j}\) and \(E_{0,i}\) are measured from the minimum of the PESs of the ith and jth electronic states, respectively, which usually differ slightly from energies calculated at the equilibrium geometry. Numerical details for the estimation of \(E_{0,j}\) can be found in Sec III. The total relaxation rate of an electron (hole) state through
electron-phonon interaction is expressed as the sum of all downward (upward) decay rates

\[ \gamma_i^{\rightarrow \rho} = \sum_{j} W_{i \rightarrow j} \]  \hspace{1cm} (36)

It should be pointed out wherein that the adiabatic approximation and the perturbation approximation discussed above are just a crude model of the system. A more accurate description for the PES of the system needs to move from the adiabatic picture to the diabatic picture by a unitary transformation of adiabatic electronic wavefunctions. In this paper, however, we still estimate the non-radiative decay rates of electrons and excitons within the adiabatic picture for the following reasons. First, a practical MEG system contains dozens of atoms or even more, which correspond to vibrational modes at the order of $10^2$ and excitonic states at the order of $10^3$. Determining the PES accurately for the system with such a scale is computationally infeasible. Second, the failure of the adiabatic picture mostly arises from those large vibronic coupling terms $\langle \Phi_j | \partial / \partial Q_k | \Phi_i \rangle$, which make it problematic to neglect the off-diagonal elements $H_{ij}^\dagger (Q)$. However, according to Eq. (30), a large $\langle \Phi_j | \partial / \partial Q_k | \Phi_i \rangle$ leads to an artificially large nonradiative relaxation rate $W_{i \rightarrow j}$, which will be neglected in the MEG analysis, since only small $W_{i \rightarrow j}$ are counted. This means the problematic states are always excluded automatically and shall not change significantly the data analysis.

### III. NUMERICAL IMPLEMENTATIONS

The ground state LDA calculation is performed using the SIESTA code. Core electrons [1s²2s²2p⁶] of Si are replaced by the nonlocal norm-conserving pseudopotential based on the Troullier-Martins scheme. A triple-ζ polarization (TZP) basis set of numerical atomic orbitals is used for the valance electrons of Si. The optimized structure of Si₂₆ is illustrated in Fig. 2a, which is consistent with the result reported in Ref. 31. The optimized structure of Si₄₆ is shown in Fig. 2b, which is obtained by merging two Si₂₆ together, with the central hexagonal ring shared. Any major difference in the results can be mostly attributed to the size effect, since both Silicon clusters have the C₂v symmetry, and their structures are quite similar.
FIG. 2. Optimized structures of Si_{26} and Si_{46}. The labels in brackets correspond to the point group symmetries of the clusters.

All integrals are evaluated on a uniform grid in real space with grid spacing of 0.5 a.u.. The exchange integrals \( \int \int d\mathbf{r} d\mathbf{r}' \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) V(\mathbf{r}, \mathbf{r}') \varphi_k(\mathbf{r}') \varphi_l(\mathbf{r}') \) are evaluated by first solving Poisson equations with the multigrid method. The convergence of the QP calculation usually requires a large number of unoccupied states for the evaluation of the polarizability. Thus a Coulomb-hole screened-exchange (COHSEX) remainder scheme has been applied to accelerate the convergence of the correlation part \( \langle \varphi | \Sigma_c | \varphi \rangle \). The TZP basis set has been tested to evaluate the influence of the completeness of the basis set for the GW simulations of the clusters in the investigation, and the applicability of the basis set was validated. The normal coordinates \( Q \) and frequencies \( \omega \) are obtained by diagonalizing the mass-weighed Hessian matrix. The second order derivatives \( \partial^2 U / \partial X_i \partial X_j \) are calculated by finite difference approach. Where, \( X_i \) are nuclear Cartesian coordinates. A unitary matrix is used to transform the Hessian matrix to a block diagonal matrix with each block corresponding to an irreducible representation. Block off-diagonal elements are small and thus eliminated to ensure that each \( Q \) belongs to one irreducible representation exclusively.

The force on the \( i \)th atom due to the \( j \)th electronic state is calculated as \( f_i^j \) by a modified version of the SIESTA code, which sums up all the energy derivatives associated with \( j \)th electronic state, namely those from kinetic energy, non-local pseudopotential energy, Hartree energy, exchange-correlation energy and basis overlap. Then the shift of the \( i \)th atom due to the \( j \)th electronic state is estimated as
\[ \Delta X_{i,n} = \frac{f_{i,n}^{j}}{\partial^{2}U/\left(\partial X_{i,n}\right)^{2}}, \quad n = 1, 2, 3 \quad (37) \]

Therefore the shift along kth normal coordinate due to the jth electronic state \(\Delta Q_{k}^{j}\) can be obtained by the inner product between \(\Delta X^{j}\) and \(Q_{n}\), where \(Q_{n}\) is the vector representation of \(Q_{k}\) in terms of Cartesian coordinates. We do not take into account the Jahn-Teller effect, since the two silicon clusters investigated in this paper do not have degenerate electronic states. Neither we consider the pseudo-Jahn-Teller effect, which is accompanied with large coupling \(\partial Q_{k}/\partial \Phi_{j}\) and will be neglected during data analysis. Therefore we only need to calculate those \(\Delta Q_{k}\) belonged to the irreducible representation with total symmetry, namely \(A_{1}\) of \(C_{2v}\).

By taking the equilibrium geometry \(Q\) as the origin for all normal coordinates, we have

\[ Q_{0,k}^{j} = \bar{Q}_{k} + \Delta Q_{k}^{j} \quad (38) \]

and

\[ Q_{0,k}^{j} - Q_{k}^{0,j} = \Delta Q_{k}^{j} - \Delta Q_{k}^{i} \quad (39) \]

which can be used for the calculation of \(\Delta_{k}^{i,j}\) and \(E_{M}^{i,j}\).

\(E_{0,j}^{i}\) is estimated as

\[ E_{0,j}^{i} = E^{i} - \frac{1}{2} \sum_{k} M_{k} \omega_{k}^{2} \left(\Delta Q_{k}^{j}\right)^{2} \quad (40) \]

\[ \langle \Phi_{j} | \partial Q_{k}^{j} | \Phi_{i} \rangle \] is calculated based on perturbation theory to the second order,

\[ \langle \Phi_{j} | \partial Q_{k}^{j} | \Phi_{i} \rangle = \frac{\langle \Phi_{j} | V_{local}^{i} | \Phi_{i} \rangle}{E_{i}^{i} - E_{j}^{j}} \quad (41) \]

Where we only take into account the internal conversion and neglect the intersystem crossing between singlet and triplet states due to the spin-orbit coupling. Within the pseudopotential scheme,

\[ V = V_{local} + V_{non-local} \quad (42) \]

The derivation and numerical treatment of excitonic states are similar to those of electronic states. First the force on the ith atom due to the jth excitonic state is calculated as
\[ F_i' = \sum_{v,\varepsilon} |R_{v,\varepsilon}^i|^2 (f_i' - f_i^v) \]  

(43)

from which \( \Delta X_{i,\varepsilon}, \Delta Q^i \), \( \Delta_i^j \) and \( E_{Mi}^i \) can be obtained in exactly the same manner as in the case of electrons. The coupling term between the two excitonic states is approximated as

\[
\left\langle \rho_i \left| \frac{\partial}{\partial Q_j} \right| \rho_i \right\rangle = \sum_{v,\varepsilon} \sum_{v',\varepsilon'} R_{v,\varepsilon}^i R_{v',\varepsilon'}^i \left( \delta_{v,v'}^i \left\langle \varphi_i \left| \frac{\partial V}{\partial Q_j} \right| \varphi_i \right\rangle + \delta_{\varepsilon,\varepsilon'}^i \left\langle \varphi_i \left| \frac{\partial V}{\partial Q_j} \right| \varphi_i \right\rangle \right) / (\nu - \nu')
\]

(44)

Then Eq. (30) can be extended to the calculation of excitonic nonradiative transition rates.

IV. RESULTS AND DISCUSSIONS
A. Electronic relaxation rates and MEG Features in Si clusters

The inelastic scattering rates \( \gamma^{ee} \) of electrons and holes in clusters Si26 and Si46 calculated by Eq. (8) are plotted versus the excitation energy \(|E_i - E_F|\) in log-log style in Fig. 3a and b. Note that all relaxation rates in this paper are given in unit eV, which can be easily converted to \( s^{-1} \) via being divided by \( h = 0.658 \text{ eV} \cdot \text{s} \). Both Fig. 3a and b can be roughly divided into two energy regimes. In the high-energy regime \((|E_i - E_F| > 6.0 \text{ eV})\), inelastic scattering rates \( \gamma^{ee} \) of electrons in both clusters are very close, so do \( \gamma^{ee} \) of holes. Actually the electrons and holes in the high-energy regime approach the quadratic law derived by Quinn and Ferell\(^{37}\) for the hot electrons with low excitation energies in a high-density free electron gas (FEG)

\[ \tau_i^{ee} = 2633r_s^{-5/2} (E_i - E_F)^2 \text{ eV}^2 \text{ fs}. \]  

(45)

where \( \tau_i^{ee} \left[ (2\gamma_i^{ee})^{-1} \right] \). Although silicon clusters are finite structures with electronic features of semiconductor, the law still works strikingly well in the high-energy regime. This is consistent with our previous study of Si20,\(^{14}\) where more discussion about the similarity of silicon and jellium model can be found. Similar to Si20,\(^{14}\) the scaled lifetimes \( \tau_i^{ee} (E_i - E_F)^2 \) of electrons and holes in Si26 and Si46 in this energy regime are again found to be close to the values in the bulk silicon obtained by the GW method.\(^{38,39}\) This indicates that \( \gamma^{ee} \) of electrons and holes in silicon clusters in the high-energy regime is essentially size-independent.

In the low-energy regime, on the other hand, the inelastic scattering rates of electrons and holes are found to be size-dependent in two facets. Firstly and noticeably, the minimum excitation energy required for sensible inelastic scattering in Si46 is smaller than that in Si26. It means that increasing cluster size can reduce the
threshold energy of inelastic scattering and thus cover wider energy regime. Secondly, in the energy regime covered by both clusters, the larger cluster usually exhibits higher inelastic scattering rates, especially for electrons. Both effects can be understood with the fact that the inelastic scattering rate of an electronic state in the low-energy regime is quite sensitive to the number of states between itself and the Fermi level, namely those states available for its decay transitions. As the cluster size shrinks, the number of energy levels around the Fermi level decreases dramatically, which leads to diminishing or even vanishing inelastic scattering rates for states close to the Fermi level.

![Graph of inelastic scattering rates](image)

Fig. 3 Inelastic scattering rates $\gamma^{e-e}$ of electrons and holes in (a) Si$_{26}$ and (b) Si$_{46}$ (right figure).

The nonradiative relaxation rates $\gamma^{e-p}$ of electrons and holes in clusters Si$_{26}$ and Si$_{46}$ at 0 K obtained by Eq. (30) are plotted versus the excitation energy $|E_i - E_F|$ in Fig. 4a and c. The ratios $\gamma^{e-e}/\gamma^{e-p}$ are given in Fig. 4 b and d for comparison. According to Fig. 4a and c, the patterns of the electronic nonradiative relaxation rates in both clusters are quite dispersive and no energy-dependence can be observed. The reason is that $\gamma^{e-p}$ is a local quantity in terms of energy and irrelevant to the absolute excitation energy $|E_i - E_F|$, since nonradiative relaxation can only occur between a state and those states below it while not too far (within the maximum phonon energy). This distinguishes notably from inelastic scattering, which in principle can occur between a state and those states below it while not too close
(beyond the minimum exciton energy), and absolute excitation energy $|E_i - E_f|$ does matter.

The patterns of the ratios $\gamma^{p\to e}/\gamma^{e\to p}$ in Fig. 4b and d are also quite dispersive, with some data points well above unity and some well below. This implies that inelastic scattering is highly possible to occur for some states, while nonradiative relaxation dominates the others. However, considering that nonradiative relaxation progresses in a cascade way, an electronic state with high excitation energy may eventually decay to some states favoring inelastic scattering and goes through this pathway. Therefore it is reasonable to assume that inelastic scattering can always occur for electronic states with high excitation energy, which can be regarded to be size independent based on the patterns in Fig. 4b and d. On the other hand, the size effect does manifest itself for electronic states with low excitation energy, because the energy threshold for $\gamma^{p\to e}/\gamma^{e\to p} > 1$ is lower in the larger cluster, which is consistent with the lower energy threshold of inelastic scattering in Si46 than that in Si26.

Fig. 4(a) Nonradiative relaxation rates $\gamma^{p\to e}$ at 0 K and (b) the ratio $\gamma^{p\to e}/\gamma^{e\to p}$ of electrons and holes in Si26. (c) $\gamma^{p\to e}$ at 0K and (d) $\gamma^{p\to e}/\gamma^{e\to p}$ in Si46.

The temperature effect is investigated by recalculating $\gamma^{p\to e}$ and $\gamma^{p\to e}/\gamma^{e\to p}$ at
300 K for both clusters. The results are illustrated in Fig. 5 a-d. Where we assume that the electronic scattering rates are temperature-independent and all changes arise from the temperature dependence of $\gamma^{-p}$. As temperature rises from 0 to 300 K, all $\gamma^{-p}$ are enhanced with factors ranging from 2 to 20. This reduces the ratios $\gamma^{-e} / \gamma^{-p}$, and deteriorates MEG performance of the two silicon clusters. Yet the conclusions about the size-independence in the high-energy regime and the size-dependent energy-threshold still hold.

With the results above, we can conclude that clusters with larger sizes could be better for MEG effect of electronic states (one-particle states), since they can cover broader energy range with lower MEG energy-threshold. It should be emphasized that all electronic states discussed correspond to the charge-non-conserved one-particle excitations (N->N±1), where N is the initial number of the electrons in the system investigated. These electronic states only can be generated by introducing an extra electron (N+1) or hole (N-1) into the system. For photon energy harvesting, however, only incident photons with energy larger than 7 eV are energetic enough to generate a hole state with $|E_i - E_f|$ larger than 3 eV and exhibit sensible MEG effect. This photon energy threshold lies far above the peak energy of the solar radiation spectrum and the part of solar energy above this is negligible. Therefore the MEG process based on one-particle excitations is not practical for efficiency enhancement of any solar cells. Actually in photovoltaic systems based on SCNCs, most incident photons just induce neutral excitonic (electron-hole) excitations (N->N). Therefore the MEG effect of excitons is of greater importance, which will be addressed in the next subsection.
Fig. 5(a) Nonradiative relaxation rates $\gamma^{e-p}$ at 300 K and (b) the ratio $\gamma^{e-e}/\gamma^{e-p}$ of electrons and holes in Si26. (c) $\gamma^{e-p}$ at 300K and (d) $\gamma^{e-e}/\gamma^{e-p}$ in Si46.

B. Excitonic relaxation rates and MEG Features in Si clusters

The inelastic scattering rates $\Gamma^{e-e}$ of excitons in clusters Si26 and Si46 calculated by the approximation method Eq. (13) are plotted versus the excitation energy $\Omega$, in log-log style in Fig. 6 a and b. The inelastic scattering rates $\Gamma^{e-e}$ of the larger cluster are less dispersive, and are fitted by a simple rational function (Padé function $P_2$)

$$y = 2x + a + \frac{b}{x+c}$$

where $x$ and $y$ represent $\ln(\Omega/eV)$ and $\ln(\Gamma/eV)$ respectively. The fitted curve is shown as the solid line in Fig.6b, with the fitting coefficients $a$, $b$ and $c$ as -4.73, -0.60 and -0.22. The factor of the linear term is fixed to be 2, since it is easy to prove that the quadratic relation between the excitonic decay rate and the excitonic energy is approached at high-energy limit (large $x$), provided that the quadratic relation between the QP decay rate and the QP energy is approached at high energy regime as in the two clusters simulated in this paper.

The same curve is also plotted in Fig. 6a to facilitate the comparison of the two patterns. Again we find both patterns can be roughly divided into two energy regimes. In the high-energy regime ($\Omega > 6.0$ eV), inelastic scattering rates $\Gamma^{e-e}$ of excitons
in both clusters are very close, indicating the size-independent excitonic MEG rates in this regime. In the low-energy regime, however, inelastic scattering rates $\Gamma^{e-e}$ in Si26 deviate downward from the solid line, and the lower the excitonic energy, the more significant deviation. This means the size effect also manifests itself in the excitonic MEG rates in the low-energy regime, where the larger cluster has faster MEG rates.

![Graph](image)

Fig. 6 Inelastic scattering rates $\Gamma^{e-e}$ of electrons and holes in (a) Si26 and (b) Si46 (right figure).

The nonradiative relaxation rates $\Gamma^{e-p}$ of excitons in the clusters Si26 and Si46 at 0 K obtained by Eq. (30) are plotted versus the excitation energy $\Omega_i$ in Fig. 4a and c. Significant differences can be found by comparing $\Gamma^{e-p}$ in Fig. 4 and $\gamma^{e-p}$ in Fig. 7.

Firstly, those states with small nonradiative relaxation rates, which can be found for electrons, no longer exist for excitons. The results imply that the absolute phonon bottleneck does not apply for excitonic states, since all of them decay at rather faster rates. Secondly, nonradiative relaxation rates of excitons in silicon clusters are energy-dependent and exhibit strong size-dependence in the whole energy regime. The full picture of the complicated MEG phenomenon in silicon clusters can be briefly summarized as: both of the two competing processes, inelastic scattering and nonradiative relaxation, are size- and energy-dependent for excitons with excitation energy less than 6.0 eV, which correspond to most photons in solar radiation.

Similar to $\gamma^{e-e}/\gamma^{e-p}$ of electrons, the ratios $\Gamma^{e-e}/\Gamma^{e-p}$ of excitons in Si26 and Si46 are plotted in Fig. 7b and d, where we find that $\Gamma^{e-e}/\Gamma^{e-p}$ of all excitonic states in the two clusters are less than unity, even for those excitonic states with the smallest nonradiative relaxation rates. The results indicate that nonradiative relaxation process is the dominant relaxation pathway for every single excitonic state in the silicon clusters. However, it should be emphasized that excitonic relaxation does not
necessarily correspond to poor MEG performance, since nonradiative relaxation progresses in a cascade way. Thus the MEG process can occur at each intermediate state, and the overall MEG effects of high-energy excitons may still be significant.

We thus suggest using the ratios $\Gamma_{e-p}/\Gamma_{e-e}$ for the comparison of the relative MEG performances of the two clusters. According to Fig. 7b and d, the maximum ratio in Si26 is larger than that in Si46. In addition, the smaller cluster possesses more states with $\Gamma_{e-e}/\Gamma_{e-p}$ above 0.01, and this advantage will become more significant if we consider the percentage of these states over the total states. The results imply that the MEG performance does depend on cluster size, and the smaller cluster shall be better than the larger one due to slower nonradiative relaxation of excitons. Therefore, in spite of the failure of the absolute phonon bottleneck, the relative phonon bottleneck is still valid. Besides the size-dependence, $\Gamma_{e-e}/\Gamma_{e-p}$ are also found to be slightly energy-dependent, and in general increase with increasing excitonic energy in both clusters. Based on Fig. 6 and Fig. 7, two qualitative relations about size- and energy-dependence of $\Gamma_{e-e}$ and $\Gamma_{e-p}$ can be summarized as:

Size-dependence: $\Gamma_{e-p} > \Gamma_{e-e}$,

Energy-dependence: $\Gamma_{e-p} < \Gamma_{e-e}$.

Fig. 7(a) Nonradiative relaxation rates $\Gamma_{e-p}$ at 0 K and (b) the ratio $\Gamma_{e-e}/\Gamma_{e-p}$ of
excitons in Si₂₆. (c) \( \Gamma^{e-p} \) at 0K and (d) \( \Gamma^{e-e}/\Gamma^{e-p} \) in Si₄₆.

The temperature effect is studied by recalculating \( \Gamma^{e-p} \) and \( \Gamma^{e-e}/\Gamma^{e-p} \) at 300 K for both clusters. The results are illustrated in Fig. 8a-d, with the assumption of temperature-independence of \( \Gamma^{e-e} \). When temperature rises from 0 to 300 K, ratios \( \Gamma^{e-e}/\Gamma^{e-p} \) of all excitons in the two clusters decrease, corresponding to deteriorated MEG performance. Yet all conclusions at 0 K are still valid.

For elucidating the remarkable differences between the MEG features of electronic states and excitonic states, density of states (DOS) of electrons and holes in the two clusters are plotted in Fig.9a, and those of excitons in Fig.9b. It can be seen from Fig. 9a that the electronic densities are around several dozens, and increase only moderately as the cluster size increases. In fact the DOS is approximately linear to the number of electrons \( M \), or the cluster size. The excitonic densities, however, are around several hundreds, which is about one order of magnitude higher than electronic densities. They also present stronger size-dependence than electronic densities with increasing cluster size. These observations can be attributed to fact that
the space of excitonic states is the direct product of hole space and electron space, and thus its quantity shall be proportional to $M^2$, instead of $M$. Therefore it is this substantial difference between the exponential factors for electrons (linear) and excitons (quadratic) that results in the qualitative differences between the MEG characteristics of electrons and excitons.

![Graph showing density of states for different materials](image)

Fig. 9(a) Density of states (DOS) of electrons and holes in Si26 and Si46, (b) DOS of excitons in Si26 and Si46.

V. CONCLUSION

We have calculated the electronic inelastic scattering rates $\gamma^{\text{ee}}$ in Si26 and Si46 using the many-body Green’s function theory. In general, higher excitation energy corresponds to larger $\gamma^{\text{ee}}$. In the high-energy regime, electron (hole) states in the two clusters with the same excitation energy have close $\gamma^{\text{ee}}$. In the low-energy regime, however, $\gamma^{\text{ee}}$ in the larger cluster are usually larger. Furthermore, with more states around the Fermi level, the larger cluster exhibits lower energy threshold of $\gamma^{\text{ee}}$. We have also simulated the electronic nonradiative relaxation rates $\gamma^{\text{ep}}$ at 0 K
in the two silicon clusters by the Fermi’s golden rule. The results indicate that \( \gamma^{e-p} \)
in the two clusters are quite dispersive. Therefore the multiple exciton generation (MEG) performance of electronic states, which is characterized by the ratio \( \gamma^{e-e}/\gamma^{e-p} \), is predicted to be size-independent in the high-energy regime due to the wide dispersion of \( \gamma^{e-e}/\gamma^{e-p} \). Yet the size-effect can still be observed as the lower energy threshold in the larger cluster, which implies that larger clusters could be better for MEG effect of electronic states due to broader energy range. At 300 K, the MEG performance of both clusters deteriorates due to increasing \( \gamma^{e-p} \) and decreasing \( \gamma^{e-e}/\gamma^{e-p} \), yet all conclusions obtained at 0 K are still valid.

The excitonic inelastic scattering rates \( \Gamma^{e-e} \) in Si26 and Si46 have been calculated within the framework of the many-body Green’s function theory. In the high-energy regime, \( \Gamma^{e-e} \) for the two clusters are close for the same excitonic energy. While in the low-energy regime, \( \Gamma^{e-e} \) in the larger cluster are usually larger. The excitonic nonradiative relaxation rates \( \Gamma^{e-p} \) at 0 K in the two silicon clusters have also been calculated in a similar way as for \( \gamma^{e-p} \). Our results show that \( \Gamma^{e-p} \) are large in all cases, and thus the concept of the absolute phonon bottleneck does not apply. Both \( \Gamma^{e-e} \) and \( \Gamma^{e-p} \) are size-dependent and energy-dependent. It is found that the energy-dependence of \( \Gamma^{e-p} \) is weaker than \( \Gamma^{e-e} \), while the size-dependence of \( \Gamma^{e-p} \) is stronger than \( \Gamma^{e-e} \). With larger ratios \( \Gamma^{e-e}/\Gamma^{e-p} \), the smaller cluster exhibits better excitonic MEG performance, indicating that the relative phonon bottleneck still holds. At higher temperature (300 K), excitonic MEG performance is reduced, while the above conclusions will not be changed.

The remarkable differences between the MEG characteristics of the electronic states and the excitonic states are analyzed by comparing the densities of states (DOS) of electrons (holes) with those of excitons. The excitonic densities are found to be one order of magnitude larger than the electronic densities, and scale up faster than the electronic densities as the cluster size increases. These are further attributed to the difference between the exponential factors, which are linear and quadratic to the number of valance electrons for electrons and excitons, respectively.

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