The Effect of Excitons on Raman Excitation Profiles in One-Dimensional Systems

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***Abstract*— We use the Kramers-Heisenberg approach to derive a general expression for the resonant Raman scattering cross section from a one-dimensional system explicitly accounting for excitonic effects.**

I. Introduction

Raman scattering is a standard optical spectroscopy technique used to characterize the excitation spectrum of a material system. If the exciting or scattered light frequency is nearly commensurate with an electronic transition of the material, the scattered Raman signal intensity is greatly enhanced [1]. In semiconductors or insulators, resonant Raman scattering not only serves as a probe of a structure's vibrational modes, but also can provide valuable information about the nature of a material's electronic structure. Here we construct an expression for the resonant Raman scattering cross-section from a 1D system incorporating Wannier excitons as the intermediate electronic states. Specifically, we derive a general expression that is useful for analyzing the Raman scattering cross-section as a function of laser excitation energy, the resonance excitation profile (REP), from either carbon nanotubes or semiconductor quantum wires.

II. Theory

We consider a single, single wall carbon nanotube or semiconductor quantum wire illuminated by a laser beam of fixed frequency ω_l, propagation direction $\vec{q_l}$ and polarization $\vec{e}_l$. The inelastically scattered radiation propagates in direction $\vec{q_s}$ with fixed polarization $\vec{e}_s$ and is collected so that its spectral content, ω_s, may be analyzed with a spectrometer. Without loss of generality, we focus on the Stokes scattering process in which a phonon of frequency Ω_p is created in the system as a result of the interaction. Microscopically, an incident pump photon interacts with the unexcited system, creates an electronic excitation that scatters a phonon before relaxing radiatively back to its ground state by emitting a photon. We use Fermi's golden rule to determine the Stokes differential Raman scattering cross section integrated over all scattered photon wavenumbers.

$$\frac{d\sigma_{RRS}}{d\Omega} = \frac{\omega_s^3 n_s^3 n_l V_{crystal}^2}{\omega_l c^4 (2\pi\hbar)^2} \cdot |W_{i\to f}(\omega_l, \vec{e_l}; \omega_s = \omega_l - \Omega_p, \vec{e_s})|^2 \quad (1)$$

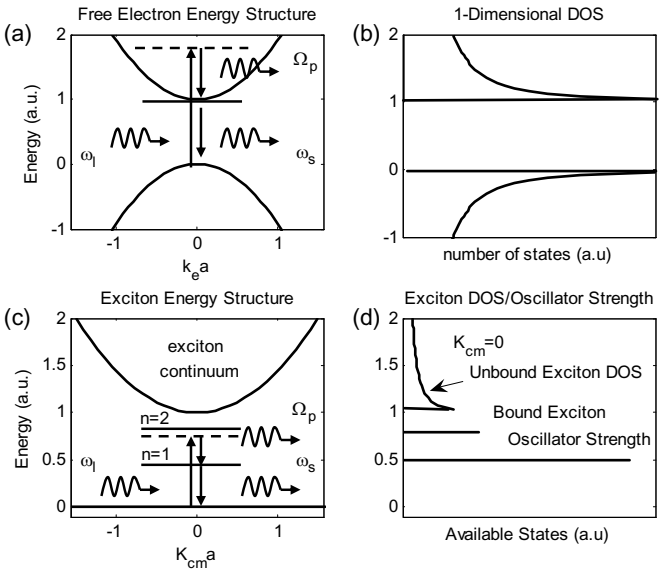

Fig. 1. The (a) free electron electronic structure, (b) the free electron density of states, (c) the excitonic electronic structure and (d) the unbound excitonic $K_{cm} = 0$ density of states and bound exciton oscillator strengths. In (a), the free electron energies are functions of the electron crystal momentum, whereas in (c), the excitonic energies are functions of the exciton center of mass momentum. The dispersion associated with the bound excitons has not been illustrated since in exciton mediated transtions, only $K_{cm} = 0$ transitions are allowed due to conservation of momentum. In addition, in (a) and (c), an outgoing Stokes resonance is illustrated where the dashed horizontal line corresponds to a virtual electronic state and a solid horizontal line corresponds to a real electronic state. In each case, a photon of energy $\hbar\omega_l$ causes an electronic transition to a virtual state, followed by the electronic excitation relaxing to a real, electronic state by emitting a phonon of energy $\hbar\Omega_p$. Finally, the electronic system returns to its ground state by emitting a photon of energy $\hbar\omega_s$. This can be compared to the free electron mediated transitions where only vertical transitons are allowed, but k_e is not constrained to be 0.

where c is the speed of light in free space, n_i is the refractive index of the material evaluated at frequency ω_i, $V_{crystal}$ is the volume of the material system and $|W_{i\to f}|^2$ is the transition probability from initial system state i, with a single pump photon, to a final state f, consisting of a single scattered photon and a single phonon. Using third order time-dependent perturbation theory, the total transition matrix element $|W_{i\to f}|^2$ from a fixed initial state to a fixed final state can be evaluated by summing over all permissible intermediate states that connect the initial and final state.

In performing this summation the intermediate electronic

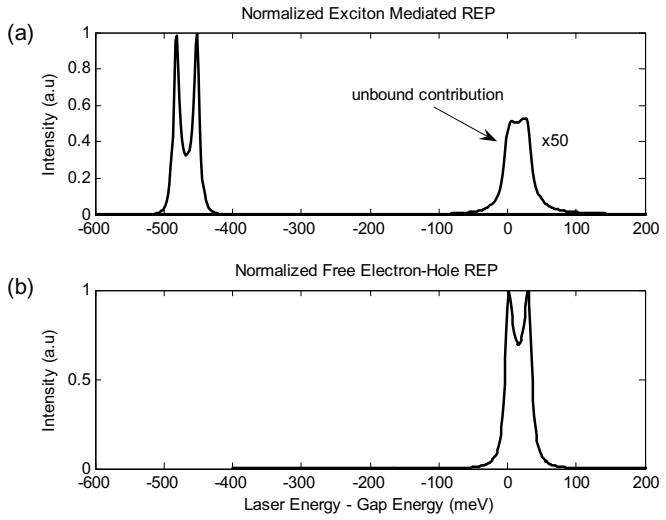

Fig. 2. Comparison of the normalized (a) exciton mediated REP with the (b) Free electron-hole mediated REP. In (a) and (b), we assume a broadening of 5 meV, an effective Rydberg of 100 meV and a phonon of energy 32 meV. In addition, in (a), we assume the ground state exciton is strongly bound. Notice in (a) the small contribution of the unbound excitons.

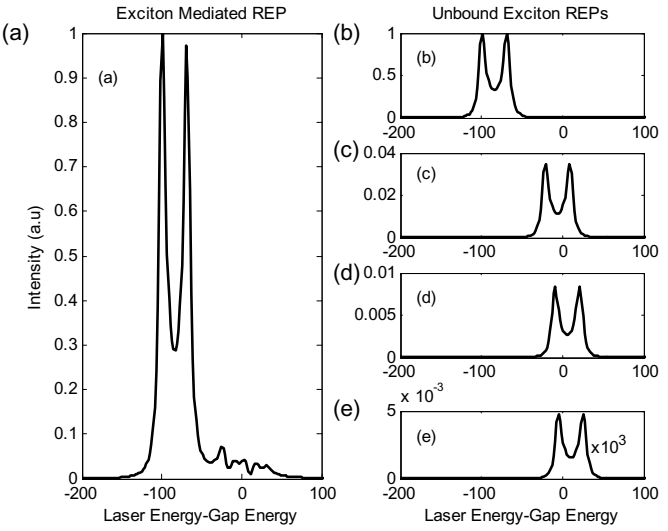

Fig. 3. The (a) exciton mediated REP and in (b)-(e), the REPs of the first four bound excitons. In (a)-(e), for a weakly bound ground state exciton, we assume a broadening of 5 meV, an effective Rydberg of 100 meV and a phonon of energy 32 meV. Notice the structure present at the location of the free electron bandgap.

excitations are treated as correlated electron-holes, or excitons, and not as free electrons and holes. Figure 1 illustrates, in a qualitative way, the change in both the electronic structure and density of states when treating the system's electronic excitations as excitons rather than free electrons and holes. Most notable, in both Fig. 1(c) and Fig. 1(d), is the appearance of bound electronic states below the bulk material system's bare energy gap.

III. Results

We use the effective mass approximation and the envelope function approximation, assuming strongly confined electrons and holes that experience identical confinement potentials, to incorporate a cutoff one-dimensional Coulomb potential, first introduced by Loudon to study the one-dimensional Hydrogen atom [3], into the Schrödinger equation to study Wannier exciton formation in one-dimensional quantum confined systems. The cutoff removes the singularity in the Coulomb potential and its size determines the depth of the potential. With the calculated exciton eignevalues and eigenstates the resultant Raman scattering cross-section can be expressed as

$$\frac{d\sigma_{RRS}}{d\Omega} \propto R|L_B(\omega_l;\omega_l-\Omega_p)+L_U(\omega_l;\omega_l-\Omega_p)|^2 \qquad (2)$$

where the cross-section splits into two seperate terms. The term L_B models scattering events mediated by intermediate bound exciton states and and the term L_U accounts for unbound exciton mediated Raman scattering.

We have studied the REP in the limits of a strong and a weakly bound ground state exciton. The gound state exciton is considered strongly bound if the cutoff parameter is much smaller than the exciton effective Bohr radius. In this limit, the Coulomb potential supports a deeply bound ground state. In Fig. 2, the REP is calculated for a strongly bound ground state exciton in (a) and for free electrons and holes in (b)[1]. Much like absorption in one-dimensional systems [2], the ground state exciton is found to dominate the Raman scattering process compared to unbound electrons and holes shown in Fig. 2(a). In addition, we find the main feature of the REP shifts its spectral location from the bare system's energy gap to the ground state exciton energy. But, in comparing Fig. 2(a) and Fig. 2(b), the qualitative lineshapes of the exciton mediated and free electron and hole REPs are similar.

In Fig. 3, we calculate the REP for a weakly bound ground state exciton. The panels (b)-(e) illustrate the conribution of the 4 lowest excitonic states to the REP. In this sitution, we find there is some modulation of the tail of the REP near the bare gap of the material system. The modulation is a result of a quantum interference between the different intermediate bound exciton states that contribute to the REP.

IV. Conclusion

We have developed a general theory for calculating the exciton mediated one phonon resonant Raman scattering cross-section for one-dimensional quantum confined systems. In studying a model two-subband system in the limit of small cutoff (strongly bound exciton), the ground state exciton dominates the 1phRRS REP and the contribution to the REP from unbound excitons with energies in the range of the single particle gap energy is quenched. As the Coulomb potential cutoff is increased, the ground state becomes more weakly bound, and we found the REP, at a fixed laser frequency, is the result of a quantum interference between all contributing intermediate excitonic pathways. The interferences lead to a complicated structure at the single particle energy gap.

References

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