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VIBRONIC TRANSITION TO A QUASI-DEGENERATED STATE: NON-ADIABATIC INTERACTION WITH PSEUDOLocal MODE

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A theory is proposed which allows one to calculate the spectrum of vibronic transitions from a non-degenerated to a quasi-degenerated electronic state in an impurity center of a crystal or in a molecule. Non-adiabatic interaction of optical electrons with the pseudolocal mode which in its turn interacts with the phonon continuum is considered.

One of the most important property of the model under consideration is the mixing of the pseudolocal mode with phonons which is described by the interaction hamiltonian

$$H' = \gamma \sum_j e_j (a_0^+ + a_0)(a_j + a_j^+) .$$

Here γ is interaction constant e_j is phonon polarization factor and a_0^+ a_j^+ are creation operators of pseudolocal mode and phonons respectively. One of the effects of this mixing is the decay of the mode, which takes place in case the frequency of the mode is in resonance with phonons.

The main goal is to calculate the optical spectrum of the transition. Restricting ourselves to the rotating wave and Condon approximations, one can show that the spectrum is

$$I(E) = \sum_{m=1,2} |\langle m|M|0g\rangle|^2 J_m(E) ,$$

where M is the electrical matrix element $|0g\rangle$ is the zeroth component ground vibronic state and $\langle m|$ m are excited electronic states, $J_m(E)$ is the Fourier transform of

$$F_m(t) = \langle 0|\hat{T} \exp[i \int_0^t d\tau H'(\tau)] e^{it(H_0+V)}|0\rangle_{mm} .$$

Using the vibronic basis of the interacting optical electron and the pseudolocal mode one can present the Fourier transform as follows

$$F_+(t) = \sum_v |C_{0v}^+|^2 \exp[iE_v^+ + g_v^+(t)] ,$$

where C_{0v}^+ and E_v^+ are eigenvectors and eigenvalues of bar vibronic Hamiltonian of the interacting optical electron, which are found numerically,

$$g_v^+(t) = \int_0^t d\tau \int_0^\tau d\tau' \Phi_v(\tau-\tau') D(\tau-\tau') ,$$

where $\Phi_v(\tau-\tau')$ and $D(\tau-\tau')$ are phonon and vibronic correlation functions respectively. The numerical calculations are in progress.