

Optical Absorption of Long Range Electron Transfer Systems in Intense Fields

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Effects of strong radiation field on long range electron transfer reactions and the crossover between the nonadiabatic and adiabatic limits are investigated. Dramatic variations of the absorption spectrum as a function of laser intensity were predicted in the nonadiabatic limit by Dakhnovskii, Lubchenko, and Coalson (*Phys. Rev. Lett.* 1996, 77, 2917). These results are extended by utilizing the interaction picture and Green function technique to calculate the spectrum in the crossover and the adiabatic regions. As the solvation timescale becomes slower, the multiphoton absorption is enhanced, and the dependence of the absorption spectrum on field intensity is suppressed, eventually vanishing in the adiabatic limit.

I. INTRODUCTION

Electron transfer (ET) reactions have been the subject of considerable experimental and theoretical study.¹⁻⁴ Effects of strong radiation field on long range ET reactions were investigated in the nonadiabatic regime.^{5,6} The ET system was modeled by the spin-boson Hamiltonian and expressions for absorption spectrum (which is closely related to ET rates because photon absorption process is associated with ET in this system.) and the equilibrium population of electronic states were derived in the nonadiabatic regime using the non-interacting blip approximation.^{7,8} The absorption spectrum $A(\mathcal{E}, \Omega)$ has been expressed as

$$A(\mathcal{E}, \Omega) = \frac{8\pi}{c\mathcal{E}^2} \sum_{l=-\infty}^{+\infty} l\Omega k_l(\mathcal{E}, \Omega), \quad (1.1)$$

where c , \mathcal{E} and Ω are the speed of light, the amplitude, and the frequency of the radiation field. k_l is the net transfer rate from the donor to the acceptor associated with l photon absorption ($|l|$ photon emission for $l < 0$). k_l was found to depend on \mathcal{E} as follows:^{5,6}

$$k_l(\mathcal{E}, \Omega) \propto J_l(a)^2, \quad (1.2)$$

where

$$a \equiv \mathcal{E} \cdot \mu_0 / \Omega, \quad (1.3)$$

$J_l(a)$ is Bessel function, and μ_0 is the difference of dipole moments between the donor state and acceptor state. It was found that the absorption spectrum $A(\mathcal{E}, \Omega)$ changes dramatically with laser intensity \mathcal{E} because the Bessel function is oscillatory and it can even vanish at certain values of a . Since the Bessel function varies considerably for $a > 1$, systems with large dipole moments are most suitable to observe

these effects. The theory was applied to mixed-valence transition metal complexes whose dipole moment μ_0 is ~ 70 D. To attain $a > 1$, \mathcal{E} needs to be larger than 10^6 V/cm. This field strength is still below the dielectric breakdown threshold in the solvent. Because of the nonadiabatic approximation, the theory cannot be applied to solvents whose solvation timescale is comparable or longer than the ET timescale. The ET timescale is estimated to be around 1 ps⁻¹ using the reorganization energy $\lambda \sim 0.1 - 1.0$ eV and the typical value of the electron tunneling matrix elements V in mixed-valence transition metal complexes, 6 meV. Many solvents have longer solvation timescales, for example, linear alcohols, propanol, butanol, pentanol whose solvation timescales are ~ 1 nsec.¹¹ In the present paper the theory^{5,6} is extended to the crossover between the nonadiabatic and the adiabatic limits. The coupling between the radiation field and the ET system is eliminated using the interaction picture. The interaction picture Hamiltonian is the same as the spin-boson Hamiltonian except that the coupling between two electronic states $V(t)$ is modulated by the radiation field

$$V(t) = V \sum_{l=-\infty}^{\infty} J_l(a) \exp [il\Omega t]. \quad (1.4)$$

It should be noted that the dependence of $V(t)$ on the amplitude \mathcal{E} is described by the Bessel function, which causes a dramatic variation of the absorption with field intensity. Using Fermi's Golden rule, which only includes the lowest order contribution in the electron tunneling matrix element V , the expression for absorption spectrum^{5,6} can be obtained in a different way. To include higher order contributions in V , the theory is applied⁹ which extends Zusman's theory¹⁰ to incorporate a complex solvation dynamics. An expression for the absorption spectrum in the crossover region is derived and is calculated numerically.

The plan of this paper is as follows: In section II the Hamiltonian in the interaction picture is calculated and a new derivation of the expression for the absorption spectrum in the nonadiabatic limit is given. In section III equations of motion for population wavepackets are derived using this Hamiltonian. The steady state solution is presented in section IV. The expression of the absorption spectrum is derived in section V and numerical calculations are presented in section VI. Finally, our results are summarized in section VII.

II. ABSORPTION SPECTRUM IN THE NONADIABATIC REGIME OBTAINED USING THE INTERACTION PICTURE

In this section we derive the expression for the absorption spectrum, by utilizing the interaction picture.

Consider a donor/acceptor system in a solvent, coupled to an external electric field. The spin-boson Hamiltonian reads

$$\hat{H}'(t) \equiv \hat{H}_0 + \mathcal{E}(t) \cdot \mu_1 |1\rangle\langle 1| + \mathcal{E}(t) \cdot \mu_2 |2\rangle\langle 2|, \quad (2.1)$$

where

$$\begin{aligned} \hat{H}_0 \equiv & E_1 |1\rangle\langle 1| + E_2 |2\rangle\langle 2| + V |1\rangle\langle 2| + V |2\rangle\langle 1| \\ & + \sum_j \left(\frac{\hat{p}_j'^2}{2m_j'''} + \frac{m_j'''\omega_j'''}{2} \hat{q}_j'^2 \right) \\ & - \hat{q}_1^{(c)} |1\rangle\langle 1| - \hat{q}_2^{(c)} |2\rangle\langle 2|. \end{aligned} \quad (2.2)$$

Here the second and third terms in Eq. (2.1) describe the coupling to the applied electric field $\mathcal{E}(t)$, $|1\rangle$ and $|2\rangle$ denote the states describing the electron on the donor site and the acceptor site, respectively. E_1 and E_2 are the corresponding electronic energies, and μ_1 and μ_2 are the permanent dipole moments.

V is the electron tunneling matrix element between these states. The fifth term in Eq. (2.2) represents the pure solvent, modeled as a continuous distribution of harmonic oscillators. \hat{p}_j''' and \hat{q}_j''' are the momenta and coordinate operators, and m_j''' and ω_j''' are the masses and the frequencies of the oscillators representing nuclear (solute and solvent) motions. The last two terms in Eq. (2.2) denote the coupling of the electron to the solvent where $\hat{q}_m^{(c)}$ are collective coordinates defined as

$$\hat{q}_m^{(c)} \equiv \sum_j m_j'''\omega_j'''^2 d_{j,m}'''\hat{q}_j''' \quad m = 1 \text{ or } 2. \quad (2.3)$$

All nuclear properties which affect the electronic motion are contained in the matrix of spectral densities $C_{mm'}(\omega)$

$$C_{mm'}(\omega) \equiv \frac{1}{2} \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle [\hat{q}_m^{(c)}(t), \hat{q}_m^{(c)}(0)] \rangle, \quad (2.4)$$

where the time-evolution of $\hat{q}_m^{(c)}(t)$ is calculated using the free nuclear Hamiltonian (the fifth term in Eq. (2.2)). The electric field $\mathcal{E}(t)$ is given by

$$\mathcal{E}(t) = \sum_j \mathcal{E}_j \cos(\Omega_j t), \quad (2.5)$$

where \mathcal{E}_j and Ω_j are the amplitude and frequency of the applied field, respectively.

We shall eliminate the last two terms in Eq. (2.1) by switching to the interaction picture. Using a unitary transformation $\hat{U}(t)$

$$\begin{aligned} \hat{U}(t) \equiv & \exp \left[-i \sum_j \left\{ \frac{a_j}{2} \sin(\Omega_j t) |1\rangle\langle 1| \right. \right. \\ & \left. \left. - \frac{a_j}{2} \sin(\Omega_j t) |2\rangle\langle 2| + \delta_j(t) \right\} \right], \end{aligned} \quad (2.6)$$

where

$$a_j \equiv \mathcal{E}_j \cdot \frac{\mu_1 - \mu_2}{\Omega_j}, \quad (2.7)$$

$$\delta_j(t) \equiv \mathcal{E}_j \cdot \frac{\mu_1 + \mu_2}{\Omega_j} \sin(\Omega_j t). \quad (2.8)$$

The Hamiltonian $\hat{H}(t)$ and the wavefunction $|\psi(t)\rangle$ in the interaction picture are given by

$$\hat{H}(t) \equiv \hat{U}^\dagger(t) \hat{H}_0 \hat{U}(t), \quad (2.9)$$

$$|\psi(t)\rangle \equiv \hat{U}^\dagger(t) |\psi'(t)\rangle \quad m = 1 \text{ or } 2, \quad (2.10)$$

where $|\psi'(t)\rangle$ is a state in the Schrodinger picture. Substituting Eqs. (2.1)-(2.8) in Eq. (2.9), we have

$$\begin{aligned} \hat{H}(t) \equiv & E_1 |1\rangle\langle 1| + E_2 |2\rangle\langle 2| + V(t) |1\rangle\langle 2| + V(t)^* |2\rangle\langle 1| \\ & + \sum_j \left(\frac{\hat{p}_j'^2}{2m_j'''} + \frac{m_j'''\omega_j'''}{2} \hat{q}_j'^2 \right) \\ & - \hat{q}_1^{(c)} |1\rangle\langle 1| - \hat{q}_2^{(c)} |2\rangle\langle 2|, \end{aligned} \quad (2.11)$$

where

$$V(t) \equiv V \exp \left[i \sum_j a_j \sin(\Omega_j t) \right] \quad (2.12)$$

$$= V \prod_j \sum_{l_j=-\infty}^{\infty} J_{l_j}(a_j) \exp [il_j \Omega_j t]. \quad (2.13)$$

Here $J_{l_j}(a_j)$ are the Bessel functions. Assuming that the solvation timescale is short compared to the ET process, the

forward and backward ET rates can be calculated to second order in the electron tunneling matrix element $V(t)$. The ET rate from the donor to the acceptor associated with 1 photon absorption $k_{11}^{(non)}$ (the ET rate from the acceptor to the donor associated with 1 photon emission $k_{12}^{(non)}$) is

$$k_{1m}^{(non)} = J_1(\mathbf{a})^2 k_m^{(non)}(-\Delta E + 1 \cdot \Omega), \quad (2.14)$$

where $\mathbf{l} \equiv (l_1, l_2, \dots)$, $\Omega \equiv (\Omega_1, \Omega_2, \dots)$, $\mathbf{a} \equiv (a_1, a_2, \dots)$, $1 \cdot \Omega \equiv \sum_j l_j \Omega_j$, $J_1(\mathbf{a}) \equiv \prod_j J_{l_j}(a_j)$, and $k_1^{(non)}(-\Delta E)$ ($k_2^{(non)}(-\Delta E)$) is the ET rate from the donor to the acceptor (from the acceptor to the donor) as a function of ΔE ($\equiv E_2 - E_1$) obtained by replacing $V(t)$ by V in Eq. (2.11). The expression of $k_m^{(non)}(-\Delta E)$ is well known.⁴ Populations of the donor P_1 and the acceptor P_2 can be calculated using the ET rates

$$P_1 = \frac{k_2^{(non)}}{k_1^{(non)} + k_2^{(non)}}, \quad (2.15)$$

$$P_2 = \frac{k_1^{(non)}}{k_1^{(non)} + k_2^{(non)}}, \quad (2.16)$$

where

$$k_m^{(non)} \equiv \sum_1 k_{1m}^{(non)}. \quad (2.17)$$

Here $\sum_1 \equiv \sum_{l_1=-\infty}^{+\infty} \sum_{l_2=-\infty}^{+\infty} \dots$. The net transfer from the donor to the acceptor associated with 1 photon absorption $k_1^{(non)}$ is

$$k_1^{(non)} = P_1 k_{11}^{(non)} - P_2 k_{12}^{(non)}. \quad (2.18)$$

The j 'th photon absorption spectrum $A_j^{(non)}(\mathcal{E}_j, \Omega_j)$ is obtained using $k_1^{(non)}$,

$$A_j(\mathcal{E}_j, \Omega_j) = \frac{8\pi}{c\mathcal{E}_j^2} \sum_1 l_j \Omega_j k_1^{(non)}. \quad (2.19)$$

These expressions extend the earlier results^{5,6} to a non-monochromatic radiation field.

III. EQUATIONS OF MOTION FOR POPULATION WAVEPACKETS

In this section the theory developed Ref. 9 is applied to investigate the crossover between nonadiabatic and adiabatic limits. A closed equation for the time evolution of the system which is not limited to the nonadiabatic limit is derived, and the steady state reached at infinite time is calculated

by solving this equation. This steady state is then used in section V for calculating the absorption spectra.

The Hamiltonian $\hat{H}(t)$ is the same as that of Ref. 9 except that the electron tunneling matrix element $V(t)$ is now time dependent. We shall derive equations of motion for population wavepackets in a similar way to Ref. 9, assuming that only low frequency modes are associated with the solvation, and the matrix of spectral densities can be described by several overdamped modes.

$$C_{mm'}(\omega) = \sum_{\alpha=1}^N 2d_{\alpha,m}d_{\alpha,m'} \frac{\Lambda_{\alpha}\omega}{\omega^2 + \Lambda_{\alpha}^2}, \quad (3.1)$$

where Λ_{α} is the relaxation rate of the overdamped α mode and $d_{\alpha,m}$ is the displacement of that mode induced in the m 'th state. We further assume that the electronic coherence relaxation timescales are much shorter than those of the populations (the spectral-diffusion limit). Eliminating the coherence we obtain

$$\begin{aligned} \frac{d\rho_{11}(\mathbf{q}, t)}{dt} = & \sum_{\alpha=1}^N \Lambda_{\alpha} \frac{\partial}{\partial q_{\alpha}} \left[(q_{\alpha} - d_{\alpha,1}) + \frac{k_B T}{2} \frac{\partial}{\partial q_{\alpha}} \right] \rho_{11}(\mathbf{q}, t) \\ & - K(\mathbf{q}) [\rho_{11}(\mathbf{q}, t) - \rho_{22}(\mathbf{q}, t)], \end{aligned} \quad (3.2)$$

$$\begin{aligned} \frac{d\rho_{22}(\mathbf{q}, t)}{dt} = & \sum_{\alpha=1}^N \Lambda_{\alpha} \frac{\partial}{\partial q_{\alpha}} \left[(q_{\alpha} - d_{\alpha,2}) + \frac{k_B T}{2} \frac{\partial}{\partial q_{\alpha}} \right] \rho_{11}(\mathbf{q}, t) \\ & - K(\mathbf{q}) [\rho_{22}(\mathbf{q}, t) - \rho_{11}(\mathbf{q}, t)], \end{aligned} \quad (3.3)$$

where \mathbf{q} is a set of overdamped modes ($\mathbf{q} = (q_1, q_2, \dots, q_N)$), $\rho_{mm}(\mathbf{q}, t)$ is a population wavepacket of the m 'th state, k_B and T are the Boltzmann constant and temperature respectively, and

$$K(\mathbf{q}) \equiv \sum_1 K_1(\mathbf{q}), \quad (3.4)$$

$$K_1(\mathbf{q}) \equiv 2\pi |V|^2 J_1(\mathbf{a})^2 \delta[U_1(\mathbf{q}) - U_2(\mathbf{q}) + 1 \cdot \Omega], \quad (3.5)$$

$$U_m(\mathbf{q}) \equiv \sum_{\alpha=1}^N [(q_{\alpha} - d_{\alpha,m})^2 - d_{\alpha,m}^2] + E_m \quad (3.6)$$

Eq. (3.5) implies that the ET process occurs only on the curve-crossing manifold \mathcal{M}_1 where

$$U_1(\mathbf{q}) - U_2(\mathbf{q}) + 1 \cdot \Omega = 0. \quad (3.7)$$

The reaction channel through the manifold \mathcal{M}_1 will be denoted 1-channel. In this reaction l_j photons with energy Ω_j are absorbed (or emitted for $l_j < 0$). We denote this 1-photon absorption. There are two differences between Eqs. (3.2)-(3.6) and those derived in Ref. 9. First here we have many reaction channels and second the electron tunneling matrix element is modified by the Bessel function of the parameter \mathbf{a} .

IV. STEADY STATE SOLUTION OF THE EQUATIONS OF MOTION

We introduce the differences $r_1(\mathbf{x}_1, t)$ between population wavepackets on the crossing manifolds

$$r_1(\mathbf{x}_1, t) \equiv \rho_{11}(\mathbf{x}_1, t) - \rho_{22}(\mathbf{x}_1, t), \quad (4.1)$$

where \mathbf{x}_1 is a vector representing a point which belongs to the curve-crossing manifold \mathcal{M}_1 . We shall derive a closed integral equation for $r_1(\mathbf{x}_1, t)$ following Ref. 9. Using the Green function we can express the solution of Eqs. (3.2) and (3.3) as

$$\begin{aligned} \rho_{11}(\mathbf{q}, t) &= \int d\mathbf{q}' G_1(\mathbf{q}, \mathbf{q}'; t) \rho_{11}(\mathbf{q}', 0) \\ &\quad - \sum_{\mathbf{I}} \int_0^t dt' \int d\mathbf{x}'_I 2\pi |V|^2 J_{\mathbf{I}}(\mathbf{a})^2 G_1(\mathbf{q}, \mathbf{x}'_I; t-t') r_1(\mathbf{x}'_I, t'), \end{aligned} \quad (4.2)$$

$$\begin{aligned} \rho_{22}(\mathbf{q}, t) &= \int d\mathbf{q}' G_2(\mathbf{q}, \mathbf{q}'; t) \rho_{22}(\mathbf{q}', 0) \\ &\quad + \sum_{\mathbf{I}} \int_0^t dt' \int d\mathbf{x}'_I 2\pi |V|^2 J_{\mathbf{I}}(\mathbf{a})^2 G_2(\mathbf{q}, \mathbf{x}'_I; t-t') r_1(\mathbf{x}'_I, t'), \end{aligned} \quad (4.3)$$

where

$$G_m(\mathbf{q}, \mathbf{q}'; t) \equiv \prod_{\alpha} G_{m\alpha}(q_{\alpha}, q'_{\alpha}; t), \quad (4.4)$$

$$\begin{aligned} G_{m\alpha}(q_{\alpha}, q'_{\alpha}; t) &\equiv \frac{1}{\sqrt{2\pi\sigma_{\alpha}(t)}} \exp \left\{ -\frac{1}{2\sigma_{\alpha}(t)} [(q_{\alpha} - d_{\alpha,m}) \right. \\ &\quad \left. - (q'_{\alpha} - d_{\alpha,m}) M_{\alpha}(t)]^2 \right\}, \end{aligned} \quad (4.5)$$

$$\sigma_{\alpha}(t) \equiv \frac{k_B T}{2} \{1 - [M_{\alpha}(t)]^2\}, \quad M_{\alpha}(t) \equiv \exp(-\Lambda_{\alpha} t), \quad (4.6)$$

and the integral $\int d\mathbf{x}_1 \dots$ is defined as

$$\int d\mathbf{x}_1 \dots \equiv \int d\mathbf{q} \delta[U_1(\mathbf{q}) - U_2(\mathbf{q}) + 1 \cdot \mathbf{\Omega}] \dots \quad (4.7)$$

Subtracting Eq. (4.3) from Eq. (4.2), we obtain a closed integral equation for r_1 ,

$$\begin{aligned} r_1(\mathbf{x}_1, t) &= S_1(\mathbf{x}_1, t) - \sum_{\mathbf{I}} \int_0^t dt' \int d\mathbf{x}'_I 2\pi |V|^2 \\ &\quad \cdot J_{\mathbf{I}}(\mathbf{a})^2 G(\mathbf{x}_1, \mathbf{x}'_I; t-t') r_1(\mathbf{x}'_I, t'), \end{aligned} \quad (4.8)$$

where

$$G(\mathbf{x}_1, \mathbf{x}'_I; t) \equiv \sum_{m=1}^2 G_m(\mathbf{x}_1, \mathbf{x}'_I; t), \quad (4.9)$$

$$\begin{aligned} S_1(\mathbf{x}_1, t) &\equiv \int d\mathbf{q}' \bar{G}_1(\mathbf{x}_1, \mathbf{q}'; t) \rho_{11}(\mathbf{q}', 0) \\ &\quad - \int d\mathbf{q}' G_2(\mathbf{x}_1, \mathbf{q}'; t) \rho_{22}(\mathbf{q}', 0). \end{aligned} \quad (4.10)$$

Since Eq. (4.8) is non local in time, it is not easy to use it for numerical calculations. By applying a Laplace transformation we obtain a local equation in the frequency domain

$$\begin{aligned} r_1(\mathbf{x}_1, s) &= S_1(\mathbf{x}_1, s) - \sum_{\mathbf{I}} \int d\mathbf{x}'_I 2\pi |V|^2 \\ &\quad \cdot J_{\mathbf{I}}(\mathbf{a})^2 G(\mathbf{x}_1, \mathbf{x}'_I; s) r_1(\mathbf{x}'_I, s), \end{aligned} \quad (4.11)$$

where the Laplace transform of $F(t)$ is denoted by $F(s)$,

$$F(s) \equiv \int_0^{\infty} dt e^{-st} F(t). \quad (4.12)$$

To calculate the absorption lineshape we need first to obtain the steady state of r at infinite time (Eq. (5.11)). Note that r does not vanish at a steady state because of the external electric field. When the external field is turned off, the system should attain thermal equilibrium at infinite time where r and the net transfer between the donor and the acceptor states vanish.⁹ We derive the expression for the steady state of r by expanding both sides of Eq. (4.11) in s , because this steady state corresponds to a $\sim s^{-1}$ term in frequency domain. We denote this steady state $r_1^{(-1)}$. The derivation is given in Appendix A. Since $S_1(\mathbf{x}_1, s)$, $G(\mathbf{x}_1, \mathbf{x}'_I; s)$, and $r_1(\mathbf{x}_1, s)$ in Eq. (4.11) contain divergent terms for $s = 0$, this equation may not be used for numerical calculations when s is small. To calculate the time evolution of the system for long times we need to remove these divergencies. The derivation is given in Appendix A. We adopt the following operator notation. A function $f_1(\mathbf{x}_1)$ and a function $F(\mathbf{x}_1, \mathbf{x}'_I)$ are expressed as a vector $|f\rangle$ and an operator \hat{F} . A set of $|\mathbf{x}_1\rangle$ is a complete orthonormal basis set

$$\langle \mathbf{x}_1 | \mathbf{x}'_I \rangle = \delta_{1,I} \delta(\mathbf{x}_1 - \mathbf{x}'_I), \quad \sum_{\mathbf{I}} \int d\mathbf{x}_1 |\mathbf{x}_1\rangle \langle \mathbf{x}_1| = 1, \quad (4.13)$$

and

$$f_1(\mathbf{x}_1) = \langle \mathbf{x}_1 | f \rangle, \quad F(\mathbf{x}_1, \mathbf{x}'_I) = \langle \mathbf{x}_1 | \hat{F} | \mathbf{x}'_I \rangle, \quad (4.14)$$

where $\delta_{1,I} \equiv \prod_j \delta_{i_j, i'_j}$ (δ_{i_j, i'_j} is Kronecker's δ), and $\delta(\mathbf{x}_1 - \mathbf{x}'_I)$ is defined as

$$\psi_1(\mathbf{x}_1) = \int d\mathbf{x}'_I \delta(\mathbf{x}_1 - \mathbf{x}'_I) \psi_1(\mathbf{x}'_I). \quad (4.15)$$

We define an inner product of $\langle 1|$ and $|f\rangle$ as

$$\begin{aligned} \langle 1 | f \rangle &\equiv \langle f \rangle, \\ \langle f \rangle &\equiv \sum_{\mathbf{I}} \int d\mathbf{x}_1 f_1(\mathbf{x}_1). \end{aligned} \quad (4.16)$$

Using this notation, Eq. (4.11) is recasted as

$$|r(s)\rangle = |S(s)\rangle - \hat{G}(s)\hat{J}|r(s)\rangle, \quad (4.17)$$

where the operators $\hat{G}(s)$ and \hat{J} correspond to the functions $G(\mathbf{x}_1, \mathbf{x}'_1; s)$ and $2\pi|V|^2 J_{1'}(\mathbf{a})^2 \delta_{1,1'} \delta(\mathbf{x}_1 - \mathbf{x}'_1)$, respectively. From Eqs. (A4), (A5), (A11), and (A12) we have

$$|r^{(-1)}\rangle = \frac{k_2}{k_1 + k_2} \hat{h}^{-1} |\bar{\rho}_{11}^{(eq)}\rangle - \frac{k_1}{k_1 + k_2} \hat{h}^{-1} |\bar{\rho}_{22}^{(eq)}\rangle. \quad (4.18)$$

where

$$\bar{\rho}_{mm}^{(eq)}(\mathbf{q}) \equiv \prod_{\alpha} \sqrt{\frac{1}{\pi k_B T}} \exp \left\{ -\frac{1}{k_B T} (q_{\alpha} - d_{\alpha,m})^2 \right\}, \quad (4.19)$$

$$k_m \equiv \langle \hat{J} \hat{h}^{-1} \bar{\rho}_{mm}^{(eq)} \rangle, \quad (4.20)$$

$$\hat{h} \equiv 1 + \hat{G}^{(0)} \hat{J}, \quad (4.21)$$

$$G^{(0)}(\mathbf{x}_1, \mathbf{x}'_1) \equiv \int_0^{\infty} dt \sum_{m=1}^2 \left[G_m(\mathbf{x}_1, \mathbf{x}'_1; t) - \bar{\rho}_{mm}^{(eq)}(\mathbf{x}_1) \right]. \quad (4.22)$$

V. THE ABSORPTION SPECTRUM

We now calculate the absorption spectrum using the steady state obtained in Section III. The net transfer rate $k_1(t)$ through 1-channel (1-channel-photon absorption rate) is

$$k_1(t) = \int d\mathbf{q} K_1(\mathbf{q}) [\rho_{11}(\mathbf{q}, t) - \rho_{22}(\mathbf{q}, t)], \quad (5.1)$$

The j 'th photon absorption spectrum $A_j(\mathcal{E}_j, \Omega_j, t)$ can be expressed using $k_1(t)$,

$$A_j(\mathcal{E}_j, \Omega_j, t) = \frac{8\pi}{c\mathcal{E}_j^2} \sum_1 l_j \Omega_j k_1(t). \quad (5.2)$$

Recasting Eqs. (5.1) using the notation of section III, we have

$$k_{1'}(t) = \langle \delta_{1',\hat{1}} \hat{J} r(t) \rangle, \quad (5.3)$$

where $\hat{1}$ is defined as

$$\langle \mathbf{x}_1 | \hat{1} | \mathbf{x}'_1 \rangle \equiv l \delta_{1,1'} \delta(\mathbf{x}_1 - \mathbf{x}'_1). \quad (5.4)$$

Since that $|r(t)\rangle$ approaches $|r^{(-1)}\rangle$ for long time, we have

$$k_{1'} \equiv \langle \delta_{1',\hat{1}} \hat{J} r^{(-1)} \rangle, \quad (5.5)$$

where

$$k_{1'} = \lim_{t \rightarrow \infty} k_{1'}(t), \quad (5.6)$$

Substituting Eq. (4.18) in Eqs. (5.5), we have

$$k_{1'} = \frac{k_2}{k_1 + k_2} k_{1'1} - \frac{k_1}{k_1 + k_2} k_{1'2}, \quad (5.7)$$

where

$$k_{1'm} \equiv \langle \delta_{1',\hat{1}} \hat{J} \hat{h}^{-1} \bar{\rho}_{mm}^{(eq)} \rangle, \quad (5.8)$$

$$= \int d\mathbf{x}_{1'} 2\pi |V|^2 J_{1'}(\mathbf{a})^2 \left[\hat{h}^{-1} \bar{\rho}_{mm}^{(eq)} \right] (\mathbf{x}_{1'}). \quad (5.9)$$

Using the rate $k_{1'm}$ we immediately calculate other rates k_m , $k_{1'}$ and the absorption spectrum $A_j(\mathcal{E}_j, \Omega_j)$ as follows: $k_{1'}$ can be calculated using Eqs. (5.7), k_m can be calculated using Eqs. (4.20) and (5.8) as

$$k_m \equiv \sum_{1'} k_{1'm}, \quad (5.10)$$

and the absorption spectrum $A_j(\mathcal{E}_j, \Omega_j) \equiv \lim_{t \rightarrow \infty} A_j(\mathcal{E}_j, \Omega_j, t)$ is finally calculated using k_1 as

$$A_j(\mathcal{E}_j, \Omega_j) = \frac{8\pi}{c\mathcal{E}_j^2} \sum_1 l_j \Omega_j k_1. \quad (5.11)$$

It should be noted that although the transfer rate $k_{1'm}$ appears to be the same as in the absence of an electric field, they are in fact different, since in this case there are couplings among many channels which are described by the inverse of the operator \hat{h} . This coupling is given by the Bessel function.

We now consider some limiting cases. First we calculate the energy absorption rate in the nonadiabatic limit. From Eqs. (4.21) and (5.8) we have

$$k_{1'm}^{(non)} \equiv \langle \delta_{1',\hat{1}} \hat{J} \bar{\rho}_{mm}^{(eq)} \rangle, \quad (5.12)$$

$$= \int d\mathbf{x}_{1'} 2\pi |V|^2 J_{1'}(\mathbf{a})^2 \bar{\rho}_{mm}^{(eq)}(\mathbf{x}_{1'}). \quad (5.13)$$

In the opposite adiabatic limit, assuming that $J_1(\mathbf{a}) \neq 0$, from Eqs. (4.21) and (5.8) we have

$$k_{1'm}^{(ad)} \equiv \langle \delta_{1',\hat{1}} \hat{G}^{(0)-1} \bar{\rho}_{mm}^{(eq)} \rangle, \quad (5.14)$$

$$= \int d\mathbf{x}_{1'} \left[\hat{G}^{(0)-1} \bar{\rho}_{mm}^{(eq)} \right] (\mathbf{x}_{1'}), \quad (5.15)$$

the net transfer rate $k_1(t)$ and the absorption spectrum are obtained using Eqs. (5.7), (5.10) and (5.11). It should be noted that in the adiabatic limit the result is independent on the strength of radiation field which is included in the operator \hat{J} . Although k_1 becomes zero on the point in the

operator \hat{J} . Although k_1 becomes zero on the point in the space of the parameter a where $J_1(a) = 0$, it is difficult to observe this effect physically. To calculate Eq. (5.8) we have to invert the kernel \hat{h} . This can be done by applying the Lanczos expansion method developed in Ref. 9. With M Lanczos collective modes we have the M -mode rate $k_{l'm}^{(M)}$,

$$k_{l'm}^{(M)} = -\frac{1}{a_{M;l'm}} \sum_{n=0}^{M-1} h_{M-1-n;l'm} a_{n;l'm}, \quad (5.16)$$

where $h_{n;l'm}$ is calculated by

$$h_{n;l'm} \equiv \langle \delta_{l',i} \hat{J} \hat{h}^n \hat{\rho}_{mm}^{(eq)} \rangle, \quad (5.17)$$

and $a_{n;l'm}$ is calculated by solving

$$h_{n'l'm} \equiv \sum_{n=1}^M h_{n'-n;l'm} a_{n;l'm} \quad (a_{0;l'm} \equiv -1). \quad (5.18)$$

In particular, in the case of single mode we have

$$k_{l'm}^{(1)} = \frac{k_{l'm}^{(non)}}{1 + \tau k_{l'm}^{(non)}}, \quad (5.19)$$

where

$$\tau \equiv \frac{\langle \delta_{l',i} \hat{J} \hat{G}^{(0)} \hat{J} \hat{\rho}_{mm}^{(eq)} \rangle}{\langle \delta_{l',i} \hat{J} \hat{\rho}_{mm}^{(eq)} \rangle^2}. \quad (5.20)$$

VI. NUMERICAL RESULTS

In this section we calculate the absorption spectra. We consider a single overdamped mode and monochromatic field and omit the subscripts of \mathcal{E}_j , Ω_j , l_j , and Λ_α . In this case the rate $k_{l'm}$ is given by

$$k_{l'm} = \frac{\pi |V|^2 J_l(a)^2}{|d_1 - d_2|} \left[\hat{h}^{-1} \hat{\rho}_{mm}^{(eq)} \right]_{l'l}, \quad (6.1)$$

where

$$x_l = \frac{E_1 - E_2 + l\Omega}{2(d_1 - d_2)}, \quad (6.2)$$

$$\left[\hat{\rho}_{mm}^{(eq)} \right]_l = \hat{\rho}_{mm}^{(eq)}(x_l), \quad (6.3)$$

$$\left[\hat{G}^{(0)} \right]_{l'l} = \int_0^\infty dt \sum_{m=1}^2 \left[G_m(x_l, x_l; t) - \hat{\rho}_{mm}^{(eq)}(x_l) \right], \quad (6.4)$$

$$\left[\hat{h} \right]_{l'l} = \delta_{l'l} + \frac{\pi |V|^2 J_l(a)^2}{|d_1 - d_2|} \left[\hat{G}^{(0)} \right]_{l'l}. \quad (6.5)$$

Here $G_m(x_l, x_l; t)$ is defined by Eqs. (4.4)-(4.6) and $\hat{\rho}_{mm}^{(eq)}$ is given by Eq. (4.19). We first perform the integration of r.h.s. of Eq. (6.4) numerically, and upon substituting Eq. (6.4) in Eq. (6.5) we obtain the matrix \hat{h} . The dimensionality of the matrices $\hat{G}^{(0)}$ or \hat{h} is determined by the number of channels that should be included in numerical calculations. The rate $k_{l'm}$ is obtained by substituting \hat{h}^{-1} in Eq. (6.1). Other rates and the absorption spectrum are calculated by substituting this rate $k_{l'm}$ in Eqs. (5.7), (5.10) and (5.11). The absorption spectra $A(\mathcal{E}, \Omega)$ calculated by varying a for several nuclear relaxation rates are shown in Fig. 1. The following parameters were used. Temperature is 300 K. The reorganization energy λ ($= |d_1 - d_2|^2$) and the free energy gap ΔG ($= E_2 - d_2^2 - E_1 + d_1^2$) are 1 eV ($d_1 = 0$, $d_2 = 1 \text{ eV}^{1/2}$, $E_1 = 0$, $E_2 = 2 \text{ eV}$). Electronic tunneling matrix element V is $0.5 \times 10^{-2} \text{ eV}$. Nuclear relaxation rate Λ is varied from 1 fs^{-1} to 1 ps^{-1} . The characteristic non-adiabatic ET time is 1 ps for these parameters. The figure

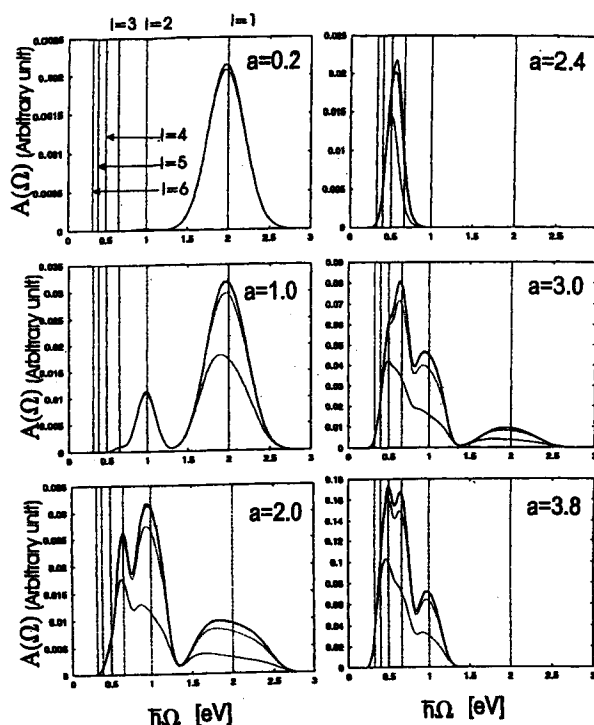


Fig. 1. Absorption spectrum $A(\mathcal{E}, \Omega)$. a is varied from 0.2 to 3.8. Temperature is 300 K. The reorganization energy λ and the free energy gap ΔG are 1 eV. Electronic tunneling matrix element V is $0.5 \times 10^{-2} \text{ eV}$. Nuclear relaxation rate Λ is varied. Solid line - $\Lambda = 1000 \text{ ps}^{-1}$. Dashed line - $\Lambda = 100 \text{ ps}^{-1}$. Short dashed line - $\Lambda = 10 \text{ ps}^{-1}$. Dotted line - $\Lambda = 1 \text{ ps}^{-1}$. The dash dotted lines are the expected peak positions of the multiphoton absorption bands and l is the number of absorbed photons.

shows that the absorption intensity is smaller and the multiphoton absorption is enhanced for slower nuclear relaxation rates. This may be understood as follows: The characteristic time of ET through l -channel by nonadiabatic regime is proportional to $J_l(a)^2$. As a result, when $|J_l(a)|$ is smaller, ET through l -channel is less saturated.

VII. SUMMARY

The expression for the absorption spectrum of a long range nonadiabatic ET system driven by a strong monochromatic field obtained in Refs. 5, 6 was rederived in a new way using the interaction picture, and extended to a non-monochromatic field. The expression was further extended to the crossover between the nonadiabatic and adiabatic limits using the theory developed in Ref. 9. The dramatic variations of the absorption spectrum shown in Ref. 5, 6 disappears in the adiabatic limit. Numerical calculation of the absorption spectrum shows that the multiphoton rate is enhanced in the crossover compared to the nonadiabatic regime.

APPENDIX A: SOLUTION FOR EQ. (4.11)

In this appendix we derive the expression of the steady state $r_1^{(-1)}$ and the integral equation for r in the $s = 0$ limit.

We assume that $|r(t)\rangle$ approaches the steady state at long times. This assumption may be justified as follows: We will construct a solution of Eq. (4.17) using this assumption. Since Eq. (4.17) has a unique solution with a certain initial condition, we can assume that the constructed solution is a unique solution of Eq. (4.17). Expanding both sides of Eq. (4.17) in s and taking terms to order s^{-2} we have

$$\hat{G}^{(-1)} \hat{J} |r^{(-1)}\rangle = 0, \quad (\text{A1})$$

where

$$|r(s)\rangle \equiv \sum_{k=-1}^{\infty} s^k |r^{(k)}\rangle, \quad (\text{A2})$$

$$|S(s)\rangle \equiv \sum_{k=-1}^{\infty} s^k |S^{(k)}\rangle, \quad (\text{A3})$$

$$\hat{G}(s) \equiv \sum_{k=-1}^{\infty} s^k \hat{G}^{(k)}. \quad (\text{A4})$$

As a consequence of the assumption above we could have Eq. (A2). We have

$$\lim_{t \rightarrow \infty} G_m(\mathbf{x}_1, \mathbf{x}'_1; t) \equiv \bar{\rho}_{mm}^{(eq)}(\mathbf{x}_1). \quad (\text{A5})$$

Using Eq. (A5), Eq. (A1) is recast as

$$\langle \hat{J} r^{(-1)} \rangle = 0, \quad (\text{A6})$$

It should be noted that the total amount of transfer between the donor and acceptor states cancels in the steady state because of Eq. (A6). Taking terms in s^{-1} we have

$$|r^{(-1)}\rangle = |S^{(-1)}\rangle - [\hat{G}^{(-1)} \hat{J} |r^{(0)}\rangle + \hat{G}^{(0)} \hat{J} |r^{(-1)}\rangle]. \quad (\text{A7})$$

Using Eq. (A5) and recasting Eq. (A7), we have

$$|r^{(-1)}\rangle = \frac{1}{1 + \hat{G}^{(0)} \hat{J}} \left[P_1(0) |\bar{\rho}_{11}^{(eq)}\rangle - P_2(0) |\bar{\rho}_{22}^{(eq)}\rangle - \langle \hat{J} r^{(0)} \rangle \left(|\bar{\rho}_{11}^{(eq)}\rangle + |\bar{\rho}_{22}^{(eq)}\rangle \right) \right], \quad (\text{A8})$$

where $P_m(t)$ is

$$P_m(t) \equiv \int d\mathbf{q} \rho_{mm}(\mathbf{q}, t). \quad (\text{A9})$$

Multiplying $\langle 1 | \hat{J}$ from the left to both sides of Eq. (A8) and using Eq. (A6) we have

$$\langle \hat{J} r^{(0)} \rangle = \frac{P_1(0)k_1 - P_2(0)k_2}{k_1 + k_2}, \quad (\text{A10})$$

where

$$k_m \equiv \langle \hat{J} \frac{1}{1 + \hat{G}^{(0)} \hat{J}} \bar{\rho}_{mm}^{(eq)} \rangle. \quad (\text{A11})$$

Substituting Eq. (A10) in Eq. (A8) we obtain

$$|r^{(-1)}\rangle = \frac{1}{1 + \hat{G}^{(0)} \hat{J}} \left[\frac{k_2}{k_1 + k_2} |\bar{\rho}_{11}^{(eq)}\rangle - \frac{k_1}{k_1 + k_2} |\bar{\rho}_{22}^{(eq)}\rangle \right]. \quad (\text{A12})$$

It should be noted that $|r^{(-1)}\rangle$ does not depend on the initial condition. This is why the steady state is independent on the initial condition. Substituting Eqs. (A12) and (A10) in Eq. (4.17) we have

$$|r_0(s)\rangle = |S_0(s)\rangle - \left[\hat{G}_0(s) \hat{J} |r_0(s)\rangle + s^{-1} \hat{G}^{(-1)} \hat{J} (|r_0(s)\rangle - |r^{(0)}\rangle) + s^{-1} (\hat{G}_0(s) - \hat{G}^{(0)}) \hat{J} |r^{(-1)}\rangle \right], \quad (\text{A13})$$

where

$$|r_0(s)\rangle \equiv |r(s)\rangle - s^{-1} |r^{(-1)}\rangle, \quad (\text{A14})$$

$$|S_0(s)\rangle \equiv |S(s)\rangle - s^{-1} |S^{(-1)}\rangle, \quad (\text{A15})$$

$$\hat{G}_0(s) \equiv \hat{G}(s) - s^{-1} \hat{G}^{(-1)}. \quad (\text{A16})$$

Combining Eq. (A13) with Eq. (A5), we have

$$|r_0(s)\rangle = \hat{h}(s)^{-1} \left[|S_0(s)\rangle - \sum_{m=1}^2 |\bar{\rho}_{mm}^{(eq)}\rangle \frac{\langle \hat{J}r_0(s)\rangle - \langle \hat{J}r^{(0)}\rangle}{s} - \frac{\hat{G}_0(s) - \hat{G}^{(0)}}{s} \hat{J}|r^{(-1)}\rangle \right], \quad (\text{A17})$$

where

$$\hat{h}(s) \equiv 1 + \hat{G}_0(s)\hat{J}. \quad (\text{A18})$$

Multiplying both sides of Eq. (A17) by $\langle 1|\hat{J}\rangle$ and recasting we have

$$\langle \hat{J}r_0(s)\rangle = \frac{1}{s + k_1(s) + k_2(s)} \left[s \langle \hat{J}\hat{h}(s)^{-1}S_0(s)\rangle + (k_1(s) + k_2(s)) \langle \hat{J}r^{(0)}\rangle - \langle \hat{J}\hat{h}(s)^{-1}(\hat{G}_0(s) - \hat{G}^{(0)})r^{(-1)}\rangle \right], \quad (\text{A19})$$

where

$$k_m(s) = \langle \hat{J}\hat{h}(s)^{-1}\bar{\rho}_{mm}^{(eq)}\rangle. \quad (\text{A20})$$

Substituting Eq. (A19) into Eq. (A17) we have

$$|r_0(s)\rangle = \hat{h}(s)^{-1} \left[|S_0(s)\rangle - C(s) \sum_{m=1}^2 |\bar{\rho}_{mm}^{(eq)}\rangle - \frac{\hat{G}_0(s) - \hat{G}^{(0)}}{s} \hat{J}|r^{(-1)}\rangle \right], \quad (\text{A21})$$

where

$$C(s) = \frac{1}{s + k_1(s) + k_2(s)} \left[\langle \hat{J}\hat{h}(s)^{-1}S_0(s)\rangle + \langle \hat{J}r^{(0)}\rangle - \langle \hat{J}\hat{h}(s)^{-1} \frac{\hat{G}_0(s) - \hat{G}^{(0)}}{s} \hat{J}r^{(-1)}\rangle \right] \quad (\text{A22})$$

Eq. (A21) is applicable in $s = 0$ limit. Eq. (A21) with Eq. (A12) is the solution of Eq. (4.17).

APPENDIX B: INVERSION OF THE KERNEL USING THE LANCZOS ALGORITHM

To evaluate the r.h.s. of Eq. (5.8) we need to invert the kernel \hat{h} . This can be done by applying the Lanczos expansion developed in Ref. 9. With M Lanczos collective modes we have the rate $k_{1,m}^{(M)}$,

$$k_{abs}^{(M)} = \frac{k_2^{(M)}}{k_1^{(M)} + k_2^{(M)}} k_{abs,1}^{(M)} - \frac{k_1^{(M)}}{k_1^{(M)} + k_2^{(M)}} k_{abs,2}^{(M)}, \quad (\text{B1})$$

where

$$k_{abs,m}^{(M)} = -\frac{1}{a_{M;m}} \sum_{n=0}^{M-1} h_{M-1-n;m} a_{n;m}, \quad (\text{B2})$$

$$h_{n;m} \equiv \langle (\hat{1} \cdot \Omega) \hat{J} \hat{h}^n \bar{\rho}_{mm}^{(eq)} \rangle, \quad (\text{B3})$$

$$a_{0;m} \equiv -1 \quad (\text{B4})$$

$$h_{n';m} \equiv \sum_{n=1}^M h_{n'-n;m} a_{n;m}. \quad (\text{B5})$$

Here $k_m^{(M)}$ is calculated as

$$k_m^{(M)} \equiv -\frac{1}{a'_{M;m}} \sum_{n=0}^{M-1} h'_{M-1-n;m} a'_{n;m}, \quad (\text{B6})$$

where

$$h'_{n;m} \equiv \langle \hat{J} \hat{h}^n \bar{\rho}_{mm}^{(eq)} \rangle, \quad (\text{B7})$$

$$a'_{0;m} \equiv -1, \quad (\text{B8})$$

$$h'_{n';m} \equiv \sum_{n=1}^M h'_{n'-n;m} a'_{n;m}. \quad (\text{B9})$$

In the same manner we have the I-absorption rate,

$$k_{abs,1}^{(M)} \equiv \frac{k_2^{(M)}}{k_1^{(M)} + k_2^{(M)}} k_{abs,11}^{(M)} - \frac{k_1^{(M)}}{k_1^{(M)} + k_2^{(M)}} k_{abs,12}^{(M)}, \quad (\text{B10})$$

where

$$k_{abs,lm}^{(M)} \equiv -\frac{1}{a_{M;ml}} \sum_{n=0}^{M-1} h_{M-1-n;ml} a_{n;ml}, \quad (\text{B11})$$

$$h_{n;ml} \equiv \langle \delta_{l,1} (\hat{1} \cdot \Omega) \hat{J} \hat{h}^n \bar{\rho}_{mm}^{(eq)} \rangle, \quad (\text{B12})$$

$$a_{0;ml} \equiv -1, \quad (\text{B13})$$

$$h_{n';ml} \equiv \sum_{n=1}^M h_{n'-n;ml} a_{n;ml}. \quad (\text{B14})$$

Taking into account a single pair of Lanczos collective modes we have

$$k_{abs}^{(1)} = \frac{k_2^{(1)}}{k_1^{(1)} + k_2^{(1)}} k_{abs,1}^{(1)} - \frac{k_1^{(1)}}{k_1^{(1)} + k_2^{(1)}} k_{abs,2}^{(1)}, \quad (\text{B15})$$

$$k_{abs,l'}^{(1)} = \frac{k_2^{(1)}}{k_1^{(1)} + k_2^{(1)}} k_{abs,l'1}^{(1)} - \frac{k_1^{(1)}}{k_1^{(1)} + k_2^{(1)}} k_{abs,l'2}^{(1)}, \quad (\text{B16})$$

where

$$k_{abs,m}^{(1)} \equiv \frac{k_{abs,m}^{(non)}}{1 + \alpha_m k_{abs,m}^{(non)}}, \quad (\text{B17})$$

$$\alpha_m \equiv \frac{\langle (\hat{\mathbf{I}} \cdot \Omega) \hat{J} \hat{G}^{(0)} \hat{J} \hat{\rho}_{mm}^{(eq)} \rangle}{\langle (\hat{\mathbf{I}} \cdot \Omega) \hat{J} \hat{\rho}_{mm}^{(eq)} \rangle^2}, \quad (\text{B18})$$

$$k_{abs, l'm}^{(1)} = \frac{k_{abs, l'm}^{(non)}}{1 + \alpha_{l'm} k_{abs, l'm}^{(non)}}, \quad (\text{B19})$$

$$\alpha_{l'm} \equiv \frac{\langle \delta_{l',1} (\hat{\mathbf{I}} \cdot \Omega) \hat{J} \hat{G}^{(0)} \hat{J} \hat{\rho}_{mm}^{(eq)} \rangle}{\langle \delta_{l',1} (\hat{\mathbf{I}} \cdot \Omega) \hat{J} \hat{\rho}_{mm}^{(eq)} \rangle^2}, \quad (\text{B20})$$

$$k_m^{(1)} \equiv \frac{\langle \hat{J} \hat{\rho}_{mm}^{(eq)} \rangle}{1 + \langle \hat{J} \hat{G}^{(0)} \hat{J} \hat{\rho}_{mm}^{(eq)} \rangle / \langle \hat{J} \hat{\rho}_{mm}^{(eq)} \rangle}. \quad (\text{B21})$$

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Charge transfer; Nonlinear spectroscopy.

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