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Excitation and dissipation of interacting many-electron system

Satoshi Yokojima, GuanHua Chen [*]

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, Hong Kong

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Abstract

A new formalism based on the equation of motion for the reduced single-electron density matrix has been developed to simulate the dissipative interacting many-electron systems. The electron correlation is treated within the random phase approximation. The Markovian bath is adopted. The resulting nonradiative dissipative term is of Lindblad-like form. The formalism is applied to a butadiene molecule embedded in a liquid or solid environment, where the valence electrons are taken as the system and the nuclear vibrational modes as the bath. Various excitations are found decaying differently, e.g., different absorption peak widths are observed. © 2002 Elsevier Science B.V. All rights reserved.

Quantum dissipation is a subject of wide spread interest in many fields of physics, chemistry and materials science. Various quantum dissipation theories (QDTs) have been developed to investigate the dynamic properties of open systems. They include the Bloch–Redfield theory [1–5], Fokker–Planck equations [6–12], and Lindblad semigroup formalism [13]. The key physical quantity in all these QDTs is the reduced density operator $\hat{\rho}_S$ of the system, whose dynamics is described by the Liouville-von Neumann equation of motion,

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}_S = -\frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{\rho}_S] + \hat{R}\hat{\rho}_S, \qquad (1)$$

where $\hat{R}\hat{\rho}_S$ is the dissipation term whose form differs for different QDTs [1–19]. Since the system density matrix needs to be solved, the computa-

tional costs of all the above methods are quite expensive, and the calculations have been limited thus to the model systems. Friesner and coworkers [4] generalized the Redfield equation by decomposing the Redfield relaxation tensor, and as a result, applied the Bloch–Redfield theory to much larger systems. Recently Yan, Chen and coworkers [20] proposed the phenomenological dissipation T_1 and T_2 terms in the time-dependent Hartree–Fock (TDHF) equation of motion (EOM) for the reduced single-electron density matrix [21–23]. This new EOM may be used to study the dynamic processes of the open systems much larger than those of other approaches. The resulting EOM is nevertheless not stable numerically, which causes the difficulty in actual implementation. Further, the parameters in the two dissipation terms (T_1 and T_2) cannot be determined from the first-principles, and are to be determined by fitting experimental results. It is therefore desirable to seek an alternative or improvement so that the dissipation terms can be determined from

[*] Corresponding author. Fax: +852-2857-1586.
E-mail addresses: yokojima@yangtze.hku.hk (S. Yokojima), ghc@everest.hku.hk (G.H. Chen).

the first-principles and the numerical procedure is stable.

We present here a new formalism to simulate the electronic dynamics of open systems. Unlike the existing QDTs [1–19], the new formalism is based on the EOM for the reduced single-electron density matrix while including nonradiative quantum dissipation explicitly. The thermal bath can be the nuclei of system and/or the environment. The traditional phenomenological pure dephasing term in the EOM for the reduced single-electron density matrix is replaced by explicit quantum dissipation terms. These terms include the electron–nuclei couplings and energy/material exchanges with the environment. The new formalism can be applied to much larger systems than before. To illustrate its validity, we apply the new formalism to study the electronic dynamics of a butadiene molecule, with the nuclear vibrational modes as the thermal bath. (For the study of the molecular electronic relaxation induced by vibrational modes, see, for example, [18,24,25].)

Consider an electronic system surrounded by a thermal bath. The total Hamiltonian $\hat{H}_T$ of the system plus the bath can be expressed as

$$\hat{H}_T = \hat{H}_S + \hat{H}_B + \hat{H}_{SB}, \tag{2}$$

where $\hat{H}_S$ is the system Hamiltonian, $\hat{H}_B$ is the bath Hamiltonian, and $\hat{H}_{SB}$ describes the coupling between the system and the bath. Specifically

$$\hat{H}_S = \sum_{i,j} t_{ij} c_i^\dagger c_j + \frac{1}{2} \sum_{i,j,k,l} v_{ijkl} c_i^\dagger c_j^\dagger c_k c_l - \vec{E}(t) \cdot \sum_{i,j} \vec{\mu}_{ij} c_i^\dagger c_j. \tag{3}$$

Here $c_i^\dagger$ (c_i) is the electron creation (annihilation) operator for an orbital i. First and second terms on the RHS of Eq. (3) are the hopping terms and the electron–electron Coulomb integrals, respectively. The third term on the RHS of Eq. (3) is for the interaction between the system and the external electric field $\vec{E}(t)$, and $\vec{\mu}_{ij}$ is the dipole matrix element between two orbitals i and j. With the linear coupling approximation, the system–bath coupling $\hat{H}_{SB}$ is given by

$$\hat{H}_{SB} = \sum_{m,s} \frac{\partial \hat{H}_S}{\partial q_{ms}} \delta q_{ms}, \tag{4}$$

where q_{ms} is the displacement of atom m along the direction s. The bath term in the Hamiltonian $\hat{H}_B$ is assumed to be harmonic and given as follows,

$$\hat{H}_B = \sum_{m,s} \frac{p_{ms}^2}{2M_m} + \frac{1}{2} \sum_{m,n,s,t} V_{ms,nt} \delta q_{ms} \delta q_{nt}, \tag{5}$$

where p_{ms} is the momentum component of the mth atom along s-direction, $V_{ms,nt}$ is the effective interaction between two atoms m and n, and M_m is the mass of mth atom.

The EOM for the reduced single-electron density matrix $\rho_{ij}(t) = \mathrm{Tr}_S(\mathrm{Tr}_B(\hat{\rho}(t)) c_j^\dagger c_i)$, where Tr_S and Tr_B are the traces over the system and the bath, respectively, is found as:

$$
\begin{aligned}
\mathrm{i}\hbar \frac{\mathrm{d}}{\mathrm{d}t} \rho_{ij}(t) = {} & \mathrm{Tr}_S([\hat{H}_S, \mathrm{Tr}_B(\hat{\rho}(t))] c_j^\dagger c_i) \\
& - \frac{\mathrm{i}}{\hbar} \sum_{m_1, m_2, s_1, s_2} \int_{t_0}^t \mathrm{d}\tau \, \mathrm{Tr}_S \\
& \times \Big(\mathrm{Tr}_B \Big([\hat{F}_{m_1 s_1} \delta q_{m_1 s_1}, \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(\hat{H}_S + \hat{H}_B)(t-\tau)} \\
& \times [\hat{F}_{m_2 s_2} \delta q_{m_2 s_2}, \hat{\rho}(\tau)] \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\hat{H}_S + \hat{H}_B)(t-\tau)}] \Big) c_j^\dagger c_i \Big),
\end{aligned}
\tag{6}
$$

where

$$\hat{F}_{ms}(t) = \frac{\partial \hat{H}_S(t)}{\partial q_{ms}}. \tag{7}$$

Assuming an exponential decay for the nuclear–nuclear correlation over the time

$$
\begin{aligned}
& \mathrm{Tr}_B(\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{H}_B(t-\tau)} \delta q_{m_1 s_1} \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}_B(t-\tau)} \delta q_{m_2 s_2} \hat{\rho}_B) \\
& \simeq \exp\left(-\frac{t-\tau}{\delta\tau} \right) \mathrm{Tr}_B(\delta q_{m_1 s_1} \delta q_{m_2 s_2} \hat{\rho}_B),
\end{aligned}
\tag{8}
$$

and that $\delta\tau$ is small enough (i.e., the Markovian bath) and employing the random phase approximation (RPA) or the TDHF approximation [26], we obtain the EOM for the reduced single-electron density matrix ρ

$$
\begin{aligned}
\mathrm{i}\hbar\dot{\rho} = {} & [h, \rho] + [f, \rho] \\
& - \frac{\mathrm{i}}{\hbar} \delta\tau \sum_\nu (\rho K^\nu K^\nu + K^\nu K^\nu \rho - 2K^\nu \rho K^\nu),
\end{aligned}
\tag{9}
$$

$$h_{ij} = t_{ij} + \frac{1}{2} \sum_{k,l} (v_{ilkj} + v_{lijk} - v_{iljk} - v_{likj}) \rho_{kl}, \tag{10}$$

$$f_{ij}(t) = -\vec{E}(t) \cdot \vec{\mu}_{ij}, \tag{11}$$

$$K_{ij}^v \equiv \sum_{m,s} \frac{\partial h_{ij}}{\partial q_{ms}} \sqrt{\frac{\hbar}{2M_m\omega_v} \coth\left(\frac{\beta\hbar\omega_v}{2}\right)} Q_{ms}^v, \tag{12}$$

where $\beta = 1/k_b T$, and ω_v and Q_{ms}^v are the frequency and the mth atom's displacement along the s-direction for the vth nuclear vibrational mode, respectively. In the derivation, the nuclear–nuclear correlation $\mathrm{Tr}_B(\delta q_{m_1 s_1} \delta q_{m_2 s_2} \hat{\rho}_B)$ is calculated by assuming nuclear vibrational modes are in thermal equilibrium at a temperature T.

The detailed balance is not satisfied in Eq. (9). The energy is exchanged among the excitations, while the total number of the electrons is conserved. The parameter $\delta\tau$ can be determined from the molecular mechanics simulation. Note that although the dissipative term in Eq. (9) is of Lindblad-like form, it has very different physical meanings. Eq. (9) is the EOM for the reduced single-electron density matrix ρ not the system density matrix ρ_S. Moreover, K_{ij}^v itself depends on ρ through Fock matrix h_{ij} as in Eq. (12). It is observed that the derivatives of t_{ij} with respect to q_{ms} are much larger than those of v_{ijkl}, and we thus keep only $\partial t/\partial q$ in the evaluation of $\partial h/\partial q$ in our calculations. To the first-order, Eq. (9) becomes

$$i\hbar\delta\dot{\rho} = [h^{(0)}, \delta\rho] + [\delta h, \rho^{(0)}] + [f, \rho^{(0)}]$$
$$- \frac{i}{\hbar}\delta\tau \sum_v (\delta\rho K^v K^v + K^v K^v \delta\rho - 2K^v \delta\rho K^v), \tag{13}$$

where $\rho^{(0)}$ is the ground state reduced single-electron density matrix in the absence of the dissipation term and the external field, and $h^{(0)}$ is the corresponding Fock matrix, i.e., Eq. (10) is evaluated at $\rho_{ij} = \rho_{ij}^{(0)}$. We can show that all the induced modes in Eq. (13) decay to the ground state. As a result, it is numerically stable to solve Eq. (13).

The excitation and subsequent relaxation of 1,3-butadiene upon the incidence of an external electric pulse are investigated using the above formalism. The butadiene molecule is embedded in a liquid or solid matrix and is in thermal equilibrium with the matrix. The temperature is T. The Markovian bath approximation is thus justified

for nuclear–nuclear correlation. The PM3 Hamiltonian [27] is used for $\hat{H}_S$ and $\hat{H}_{SB}$. As for the geometry and the bath Hamiltonian $\hat{H}_B$, we found that the PM3 calculation leads to the optimized geometry and vibrational frequencies of butadiene molecule that are quite different from the experimental data [28]. It was reported that BLYP calculation resulted in the optimized geometry and vibrational frequencies that are in good agreement with the experimental ones [28]. Therefore, in this work we adopt the optimized geometry, vibrational modes and vibrational frequencies calculated by the BLYP method [29–31] with 6-311G(d,p) basis set [32]. The dipole matrix element $\vec{\mu}_{ij}$ is evaluated with the neglect of diatomic differential overlap (NDDO). The resulting 1,3-butadiene is placed in x–y plane as depicted in Fig. 1. The electric pulse is expressed as $E(t) = E_0 \exp(-t/\bar{t})^2$ with $\bar{t} = 0.1$ fs, and its polarization is along the x-direction. Eq. (13) is solved in the time domain and $\delta\tau = 0.1$ fs is used. The absorption spectrum can be obtained by Fourier transforming the induced polarization $\vec{P}(t) = \mathrm{Tr}(\vec{\mu}\delta\rho(t))$, and is plotted in Fig. 1a. The first peak appears at 4.6 eV and its half width is found to be 0.40 eV. The new formalism includes the interactions between the valence electrons and all vibrational modes. This means that the calculated half widths ΔE_{HW} correspond to both homogeneous and inhomogeneous broadenings. The 0.40 eV half width of the first peak agrees approximately with the experimental measure of ~ 0.5 eV [33]. This is the reason why the value 0.1 fs of $\delta\tau$ is adopted in the calculations. Another major absorption peak is found at 8.7 eV with a less half width of 0.31 eV. The different peak widths indicate the different decay rates of the two excitations at 4.6 and 8.7 eV. Fig. 1b shows the amplitudes of the two excitation modes versus time. The decay half time $\Delta\tau_{1/2}$ for 4.6 and 8.7 eV at temperature $T = 300$ K are 2.3 and 3.3 fs, respectively. It is verified that $\Delta E_{HW} \Delta\tau_{1/2} \sim \hbar$ for the two excitations. The decay half time of individual electronic mode is found dependent on temperature T. This is because that the nuclear motion varies with changing temperature. For example, the decay half time for the two excitations at 4.6 and 8.7 eV are 3.3 and 3.7 fs at $T = 100$ K, respectively. Note that the 4.6 eV
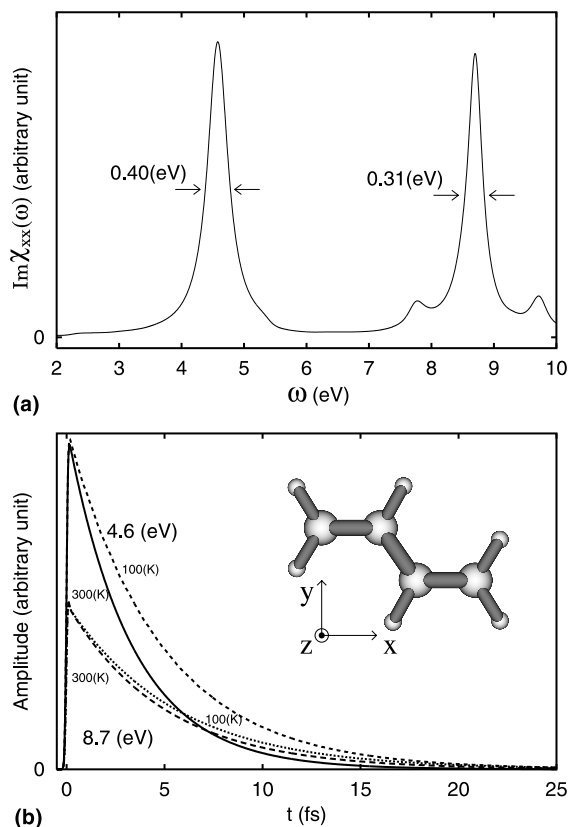
(a)

(b)

Fig. 1. (a) Absorption spectrum at $T = 300$ K; (b) shows the relaxations of the two excitations (4.6 and 8.7 eV): amplitude of the mode versus t. 1,3-butadiene is placed as shown in the inset. Solid line and long dashed line are for the 4.6 and 8.7 eV excitations at $T = 300$ K, respectively. Short dashed and dotted line are for the two excitations at $T = 100$ K, respectively.
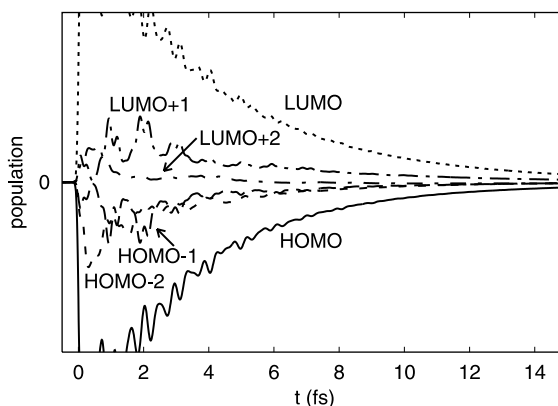

Fig. 2. The population relaxations for HOMO, LUMO, HOMO − 1, LUMO+1, HOMO − 2, and LUMO+2. The solid line (HOMO), for example, shows $\delta\rho_{\text{HOMO,HOMO}}$ versus time t in Hartree–Fock molecular orbital representation [26].

excitation is more sensitive on T, and it decays much faster than the 8.7 eV excitation as T is raised. This is because that the 4.6 eV excitation couples more strongly to the nuclear motion.

Fig. 2 shows the population relaxation after the incidence of the electric pulse. The density matrix $\delta\rho$ is mapped onto the Hartree–Fock molecular orbital representation [26], and the induced populations of the highest occupied molecular orbital (HOMO), HOMO − 1, HOMO − 2, the lowest unoccupied molecular orbital (LUMO), LUMO+1, and LUMO+2 are plotted versus the time t. The negative value indicates the depletion of the electron or the existence of holes. The induced populations of the HOMO and LUMO

(also HOMO − 1 and LUMO+1) are almost the mirror images of each other, while the populations of the HOMO − 2 and LUMO+2 are completely different. The larger numbers of induced electrons (holes) at the LUMO (HOMO) indicates the efficient transition of electrons from the HOMO to the LUMO immediately after the application of the electric pulse $E(t)$. All the induced populations (electrons or holes) decay to zero, i.e., relaxes to the ground state. The population relaxation to the ground state is due to the existence of the electron–hole (hole–electron) components of K^v.

We have shown that the new formalism can be employed to simulate the nonradiative relaxations of interacting many-electron systems that are in contact with thermal baths. Various excitations may couple differently to the thermal bath, and this is taken into account naturally by the new formalism. The simulation on the butadiene molecule is meant to be more of an illustration than a serious attempt to reproduce the details of its electronic relaxation. Our equation does not consider the large amplitude motion and photoisomerization. Those effects are beyond the scope of this work which is intended to develop and illustrate the new formalism. In the formalism, the interaction among electrons are explicitly considered. It would be interesting to quantify the effects of the electronic interaction on the relaxation

processes. Switching off the electronic interaction leads to drastically different electronic structure. This makes the direct comparison between the interacting and noninteracting electronic systems difficult. A possible solution is to starting from the noninteracting electronic system and then turn on gradually the electronic interaction while measuring the related effects. It is emphasized that this formalism is based on the EOM of reduced single-electron density matrix and is very different from the conventional QDTs that follow the dynamics of the reduced density matrix of system. Therefore, this formalism can be applied for much larger and realistic systems, as we did here. In our calculation, we include explicitly all valence electrons (total of 22 electrons) and take into account the couplings between all valence electrons and all vibrational modes. For most conventional QDTs, one solves the electronic structures first and then adds T_1 and T_2 relaxation terms phenomenologically [1,18]. In principle, the T_1 and T_2 relaxation terms can be evaluated explicitly [18]. However, because of extreme large computational resources are required, this has not been done for realistic many-electron systems [18]. Our formalism introduces for the first time the quantum chemistry methodology to simulate the dissipative many-electron systems. For the moment it employs the semiempirical Hamiltonian. We can implement easily our formalism with the first-principle quantum chemistry methods, for instance, the time-dependent density functional theory (TDDFT) [34]. This makes the first-principle simulations of open systems possible. Combined with a recently developed localized-density-matrix (LDM) method [21–23], the new formalism is expected to simulate the electronic dynamics of very large open molecular systems.

Acknowledgements

References

[1] F. Bloch, Phys. Rev. 70 (1946) 460.
[2] A.G. Redfield, Adv. Magn. Reson. 1 (1965) 1.
[3] A. Suárez, R. Silbey, I. Oppenheim, J. Chem. Phys. 97 (1992) 5101.
[4] W.T. Polland, R.A. Friesner, J. Chem. Phys. 100 (1994) 5054.
[5] J. Cao, J. Chem. Phys. 107 (1997) 3204.
[6] G.S. Agarwal, Phys. Rev. 178 (1969) 2025.
[7] G.S. Agarwal, Phys. Rev. A 4 (1971) 739.
[8] A.O. Caldeira, A.J. Leggett, Physica A 121 (1983) 587.
[9] Y. Tanimura, R. Kubo, J. Phys. Soc. Jpn. 58 (1989) 101.
[10] Y. Tanimura, Y. Maruyama, J. Chem. Phys. 107 (1997) 1779.
[11] Y.J. Yan, S. Mukamel, J. Chem. Phys. 89 (1988) 5160.
[12] Y.J. Yan, Phys. Rev. A 58 (1998) 2721.
[13] G. Lindblad, Commun. Math. Phys. 48 (1976) 119.
[14] R.P. Feynman, F.L. Vernon Jr., Ann. Phys. 24 (1963) 118.
[15] H.M. Sevian, J.L. Skinner, J. Chem. Phys. 91 (1989) 1775.
[16] J.S. Bader, B.J. Berne, J. Chem. Phys. 100 (1994) 8359.
[17] H. Dekker, Phys. Rep. 80 (1981) 1.
[18] S. Mukamel, Principles of Nonlinear Optical Spectroscopy, Oxford, New York, 1995.
[19] D. Kohen, C.C. Marston, D.J. Tannor, J. Chem. Phys. 107 (1997) 5236.
[20] H.Y. Zhang, X.Q. Li, Y.J. Yan, S. Yokojima, G.H. Chen, Chem. Phys., unpublished.
[21] S. Yokojima, G.H. Chen, Phys. Rev. B 59 (1999) 7259.
[22] S. Yokojima, G.H. Chen, Chem. Phys. Lett. 292 (1998) 379.
[23] W.Z. Liang, S. Yokojima, D.H. Zhou, G.H. Chen, J. Phys. Chem. A 104 (2000) 2445.
[24] A. Nitzan, J. Jortner, Theor. Chim. Acta 29 (1973) 97.
[25] J.G. Saven, J.L. Skinner, J. Chem. Phys. 99 (1993) 4391.
[26] A. Takahashi, S. Mukamel, J. Chem. Phys. 100 (1994) 2366.
[27] J.J.P. Stewart, J. Comput. Chem. 10 (1989) 209.
[28] C.H. Choi, M. Kertesz, S. Dobrin, J. Michl, Theor. Chem. Acc. 102 (1999) 196.
[29] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[30] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
[31] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 157 (1989) 200.
[32] M.J. Frisch et al., Gaussian 94 (Revision C.3), Gaussian Inc., Pittsburgh, PA, 1995.
[33] D.L. Phillips, M.Z. Zgierski, A.B. Myers, J. Phys. Chem. 97 (1993) 1800.
[34] E. Runge, E.K.U. Gross, Phys. Rev. Lett. 52 (1984) 997.