using the experimental value of $\Gamma = 100$ meV.[3] Both sets of experimental data fall below the semiclassical curve at high values of δ, and it is apparent that the energy shifts measured for selenium decrease faster with increasing δ than do the semiclassical predictions.

An interesting question arises concerning the effect of extra-atomic relaxation on PCI in solids. Normally, extra-atomic relaxation, associated with the adjustment of neighboring atoms to the new potential produced by the doubly ionized atom resulting from photoionization followed by Auger decay, contributes to the energy of the emitted Auger electron.[10] However, when the photoelectron remains in the near vicinity during the emission of the Auger electron, the extra-atomic relaxation contribution to the Auger electron energy may be expected to decrease. The difference between the extra-atomic relaxation energies for a singly ionized and a doubly ionized selenium atom is estimated to be of the order of 3 eV.[4] Thus, it is likely that extra-atomic relaxation will have a nonnegligible effect on the observed Auger-peak shifts in the near-threshold photoionization of these solid compounds.

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[1] See R. Morgenstern, A. Niehaus, and U. Thielmann, J. Phys. B 10, 1039 (1977), and references therein.

[2] A. Niehaus, J. Phys. B 10, 1845 (1977).

[3] V. Schmidt, N. Sandner, W. Mehlhorn, M. Y. Adam, and F. Wuilleumier, Phys. Rev. Lett. 38, 63 (1977).

[4] M. K. Bahl, R. L. Watson, and K. J. Irgollic, to be published.

[5] M. K. Bahl, R. L. Watson, and K. J. Irgollic, J. Chem. Phys. 66, 5526 (1977).

[6] As a result of a typographical error, a factor of 4 was omitted before the δ in the second term of Eq. (16) in Ref. 2.

[7] R. B. Barker and H. W. Berry, Phys. Rev. 151, 14 (1966).

[8] J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967).

[9] M. O. Krause and J. H. Oliver, to be published.

[10] D. A. Shirley, Phys. Rev. A 7, 1520 (1973).

Reduced Equations of Motion for Molecular Multiphoton Processes

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I derive reduced equations of motion for molecular multiphoton processes by constructing a set of relevant operators and adopting the Mori projection-operator technique. The intramolecular dephasing processes which play a dominant role in the quasicontinuum are properly incorporated by utilizing the representation of exact molecular states. The resulting equations include dephasing operators expressed in terms of intramolecular dipole correlation functions, and interpolate between the coherent and incoherent driving limits.

Studies of molecular multiphoton processes (MMP) induced by the interaction of infrared lasers with polyatomic molecules under collisionless conditions are providing a revolutionary new method for studying the dynamics of highly excited molecules and chemical reactions and achieving laser-controlled chemistry.[1-9] It is clear[4-9] that after the absorption of a few infrared quanta, the molecule is pumped into the quasicontinuum where the high density of molecular states changes the nature of the molecular driving from coherent to totally incoherent. Despite numerous experimental and theoretical efforts, the appropriate description of the absorption process and the nature of the quasicontinuum dynamics are not yet understood.

I present here a microscopic derivation of reduced equations of motion (REM) for MMP, starting with the complete Liouville equation. The approach is "hydrodynamiclike" and is based on the choice of a few relevant molecular operators corresponding to level populations and coherences and then making use of Mori's projection-operator technique[10] utilizing a new partial-time-ordering version.[10,11]

Consider a polyatomic molecule irradiated with a monochromatic infrared laser whose frequency is ω_L. We partition the molecular states relevant for the multiphoton excitation into groups (levels) where the nth level contains molecular states with energy around $n\omega_L$. Within the rotating-wave approximation (RWA) we need consider only the following groups of states: $|0\alpha,v\rangle$, $|1\beta,v-1\rangle$, $\ldots,|n\gamma,v-n\rangle$. Here $|n\gamma,v-n\rangle$ denotes a molecular state $|n\gamma\rangle$ (eigenstate of the true molecular Hamiltonian) dressed[12] (to zeroth order) by the radiation field with $v-n$ photons. n denotes the level, whereas γ runs over the states within the nth level. For brevity $|n\gamma,v-n\rangle$ will be denoted by $|n\gamma\rangle$. The total Hamiltonian within the RWA is

$$H=\sum_{n\alpha}|n\alpha\rangle E_{n\alpha}\langle n\alpha|+\epsilon\sum_{\substack{n,m=n\pm1\\ \alpha,\beta}}|n\alpha\rangle\mu_{\alpha\beta}{}^{nm}\langle m\beta| \equiv H_0+H'. \tag{1}$$

Here $E_{n\alpha}$ is the energy of the dressed $|n\alpha\rangle$ molecular state, i.e., $E_{n\alpha}=E_{n\alpha}{}^0-n\omega_L$, μ is the dipole operator, $\mu_{\alpha\beta}{}^{nm}\equiv\langle n\alpha|\mu|m\beta\rangle$, and ϵ is the laser field amplitude. The Hamiltonian (1) represents a set of coupled quasicontinua of dressed molecular states.

For an N-level molecular system we shall now define the following $M=3N-2$ relevant molecular operators

$$A_{nn}=(d_n)^{-1/2}\textstyle\sum_\alpha|n\alpha\rangle\langle n\alpha|, \qquad n=0,1,\ldots,N-1, \tag{2a}$$

$$A_{nm}=(\gamma_{nm})^{-1}\sum_{\alpha,\beta}\mu_{\alpha\beta}{}^{nm}|n\alpha\rangle\langle m\beta|, \qquad m=n\pm1, \tag{2b}$$

where

$$\gamma_{nm}{}^2=\sum_{\alpha\beta}|\mu_{\alpha\beta}{}^{nm}|^2 \tag{2c}$$

and d_n is the number of states in the nth level. The operators A_{nn} were chosen since they represent the primary quantities of interest (the populations of the various levels), whereas A_{nm} are related to their time derivatives ($[H,A_{nn}]$). Our operators (2) are orthonormal, i.e.,

$$\langle A_{nm},A_{n'm'}{}^\dagger\rangle\equiv\mathrm{tr}A_{nm}A_{n'm'}{}^\dagger=\delta_{nn'}\delta_{mm'}. \tag{3}$$

We now define the following Mori projection operator, P,[10] with

$$PB\equiv\sum_{n,m}\langle B,A_{nm}{}^\dagger\rangle A_{nm}.$$

Since initially the molecular density matrix commutes with P, we shall be interested only in the projection $P\rho(t)P$, which may be expanded as

$$P\rho(t)P=\sum_{n,m}\sigma_{nm}(t)A_{nm}, \tag{4}$$

where $\sigma_{nm}(t)$ are c numbers.

We definition of an M-dimensional vector, $\underset{\sim}{A}$, whose components are A_{nm} and a corresponding vector, $\underset{\sim}{\sigma}$, with components σ_{nm}, the *exact* time evolution of $\underset{\sim}{\sigma}$ is then given by[10]

$$d\underset{\sim}{\sigma}(t)/dt =-i\langle Le^{-iLt}\underset{\sim}{A},\underset{\sim}{A}^\dagger\rangle\langle e^{-iLt}\underset{\sim}{A},\underset{\sim}{A}^\dagger\rangle^{-1}\underset{\sim}{\sigma}(t), \tag{5}$$

where each bracket is an $M\times M$ matrix. L is the Liouville operator corresponding to H, i.e., $L=[H,\ ]$. We further define

$$P_n=d_n{}^{1/2}\sigma_{nn}, \tag{6a}$$

$$\omega_{\alpha\beta}=(E_{n\alpha}-E_{m\beta})-\bar{\omega}_{nm}, \tag{6b}$$

$$\bar{\omega}_{nm}=\gamma_{nm}{}^{-2}\sum_{\alpha,\beta}|\mu_{\alpha\beta}{}^{nm}|^2(E_{n\alpha}-E_{m\beta}), \tag{6c}$$

and

$$\Omega_{nm}=\epsilon\gamma_{nm}. \tag{6d}$$

P_n is the population of the nth level and Ω_{nm} is the integrated Rabi frequency for the n-m transition. Expanding the operator to the right-hand side of Eq. (5), we get the following REM:

$$dP_n/dt=-i\Omega_{n,n+1}(\sigma_{n+1,n}-\sigma_{n,n+1})-i\Omega_{n,n-1}(\sigma_{n-1,n}-\sigma_{n,n-1}), \tag{7a}$$

$$d\sigma_{nm}/dt=[-i\bar{\omega}_{nm}+G_{nm}(t)]\sigma_{nm}-i\Omega_{nm}F_{nm}(t)(P_m/d_m-p_n/d_n), \quad m=n\pm1, \tag{7b}$$

where

$$G_{nm}(t)=d\ln I_{nm}(t)/dt=I_{nm}{}^{-1}dI_{nm}(t)/dt, \tag{8}$$

$$F_{nm}(t)=I_{nm}(t)\exp(-i\bar{\omega}_{nm}t)+[i\bar{\omega}_{nm}-G_{nm}(t)]\int_0^t d\tau\, I_{nm}(\tau)\exp(-i\bar{\omega}_{nm}\tau) \tag{9}$$

or, alternatively,

$$F_{nm}(t)=-\left[\int_0^t d\tau\, I_{nm}(\tau)\exp(-i\bar{\omega}_{nm}\tau)\right]\left\{\frac{d}{dt}\ln\left[\frac{d}{dt}\ln\int_0^t d\tau\, I_{nm}(\tau)\exp(-i\bar{\omega}_{nm}\tau)\right]\right\}. \tag{9a}$$

Equations (7a) are exact. Equations (7b) are more complicated since not all possible operators of the form $[H, A_{nm}]$ are included in our basis set (2). This "reduction" results in the appearance of the depasing terms F and G. Equations (7b) were evaluated to first order in Ω.

G and F are relaxation operators expressed in terms of the *intramolecular dipole correlation functions* $I_{nm}(t)$ which are the key quantities in the present formulation and contain all the relevant molecular information,

$$I_{nm}(t) = \gamma_{nm}^{-2} \sum_{\alpha\beta} |\mu_{\alpha\beta}^{nm}|^2 \exp(-i\omega_{\alpha\beta} t)$$
$$\equiv \gamma_{nm}^{-2} \langle \mu_{nm}(t) \mu_{mn}(0) \rangle . \qquad (10)$$

By definition $I_{nm}(0) = 1$ and physically we expect $I_{nm}(\infty) = 0$. We also note that $F(0) = 1$.

The REM (7) exhibit the following features:

(1) Because of the adoption of a basis set of true molecular states, all the anharmonicities are properly (nonperturbatively) incorporated in this REM. As a result, no relaxation of population (T_1-type) terms need to be considered.

(2) Equations (7)–(10) provide us for the first time with exact *microscopic expressions* for intramolecular dephasing rates. The dephasing terms in our REM are $G_{nm}(t)$ and $F_{nm}(t)$ and they are independent of the dipole strength μ but rather depend merely on the *functional form* of the dipole operator. If we set $\Omega = 0$, we can solve for $\sigma_{nm}(t)$:

$$\sigma_{nm}(t) = \exp(-i\bar{\omega}_{nm} t) I_{nm}(t) \sigma_{nm}(0). \qquad (11)$$

I_{nm} is thus the intramolecular dipole correlation function for the n-m transition. If we adiabatically switch a weak radiation field, Eq. (7) will predict a line shape which is the Fourier transform of $I_{nm}(t)$. At the early stages of the molecular multiphoton excitation ("region I")[4-6] each level contains only one state (no reduction). In this case we have $I_{nm}(t) = F_{nm}(t) = 1$, $G_{nm}(t) = 0$, there is no dephasing, and we recover the ordinary limit of coherent driving.

(3) Within the present formulation, the dephasing arises entirely as a result of our reduced description of the molecular dynamics[13] (i.e., choice of a few variables). This is to be contrasted with ordinary line-shape formulations[14] where the dephasing is treated perturbatively in some intramolecular interaction. The conventional perturbative expressions for line broadening[14] may be obtained from our general expressions(8) and (9) by assuming a zeroth-order separation of degrees of freedom into a "system" and a "bath" whereby $\mu_{\alpha\beta}^{nm} = \mu_{nm}\delta_{\alpha,\beta}$. We then introduce an intramolecular coupling V and evaluate G and F to lowest order in V, resulting in $F_{nm}(t) \cong 1$ and

$$\operatorname{Im} G_{nm}(t) \cong -\operatorname{Im} \int_0^t d\tau \sum_{\alpha\beta} |V_{\alpha\beta}^{nn} - V_{\alpha\beta}^{mm}|^2$$
$$\times \exp(-i\omega_{\alpha\beta}\tau).$$

Neither the separation into a system and a bath nor the perturbative treatment of V is expected to hold for MMP.

(4) A reasonable form for $I_{nm}(t)$ may be[15] $I_{nm}(t) = \exp\{-(\Gamma/a)[\exp(-at) - 1 + at]\}$. This is the well-known correlation function from the theory of Brownian motion. With use of this correlation function, the dephasing term (8) assumes the form $G_{nm}(t) = -\Gamma[1 - \exp(-at)]$ and when $a \gg \Omega$ (Markovian limit), we may replace $G(t)$ in our REM by $G(\infty) = -\Gamma$ and we recover the phenomenological dephasing term.[14]

(5) There is a continuous transition to incoherent driving. Assuming $a \gg \Gamma$, we get $I_{nm}(t) = \exp(-\Gamma t)$, which gives $F(t) = 1$. Assuming further that $\Gamma \gg \Omega$ (fast dephasing), we can invoke a steady-state assumption for the coherences, and our REM assumes the form of simple rate equations corresponding to incoherent driving:

$$\dot{P}_n = \sum_{m=n\pm1} \frac{2\Gamma\Omega_{nm}^2}{\Gamma^2 + \bar{\omega}_{nm}^2} \left(\frac{P_m}{d_m} - \frac{P_n}{d_n} \right). \qquad (12)$$

The steady-state assumption for the coherences may be invoked under less restrictive assumptions than done here (i.e., assuming $a \gg \Omega$ and leaving the time dependence in F). In this case we get rate equations for the populations with time-dependent rates.

(6) The present formulation enables us to construct a closed set of REM for *any* chosen set of molecular operators. However, the complexity (and usefulness) of the REM are directly related to the choice of the right number of variables.

Equations (7) could be improved (if necessary) by two ways. We may either hold the number of operators (2) fixed, and add more terms (higher order in Ω) to the evolution operator or, alternatively, add more dynamical operators and leave the evolution operator to low order in Ω. Either approach is sufficient in principle. The systematic way to increase the number of operators is to add more derivatives (i.e., operators of the form $[H, A_{nm}]$, $[H,[H, A_{nm}]]$, etc.). As an example, we may consider the operators corresponding to multiple-quantum coherence A_{nm} (for $m - n > 1$), obtained by replacing the matrix $\underline{\mu} = (\mu)_{n\alpha, m\beta}$

in (2b) and (2c) by $\underset{\sim}{\nu}$ where $\nu_{n,m} = \mu_{n,n+1}\mu_{n+1,n+2} \cdots \mu_{m-1,m}$. The dephasing term of $I_{nm}(t)$ $[G_{nm}(t)]$ will be given again by (8) where in Eq. (10) we simply replace $\underset{\sim}{\mu}$ by $\underset{\sim}{\nu}$. In addition, we shall have complicated driving terms connecting σ_{nm} with $\sigma_{n\pm 1,m}$ and $\sigma_{n,m\pm 1}$, which may be expressed in terms of higher-order three-time intramolecular dipole correlation functions.[16] By adoption of this choice, the number of variables is N^2. It should be noted, however, that unlike conventional derivations of master equations,[9] the number N^2 does not have any special role within the present formulation. The former are based on partitioning the degrees of freedom into a "system" and a "bath" with a weak interaction. N^2 is then the size of a complete set of system operators. Since for MMP we do not have such a natural partitioning, the optimal size of the reduced description is dictated merely by the simplicity of the resulting REM, and we may adopt a convenient set of REM with significantly smaller number of variables.

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[1] See papers in *Tunable Lasers and Applications*, edited by A. Mooradian, T. Jaeger, and P. Stokseth (Springer, New York, 1976); *Multiphoton Processes, Proceedings of the ICOMP Conference*, edited by J. H. Eberly and P. Lambropolous (Wiley, New York, 1978). (A preliminary report of the present work has appeared in the abstracts of this conference.)

[2] N. R. Isenor and M. C. Richardson, Appl. Phys. Lett. 18, 224 (1971), and Opt. Commun. 3, 360 (1971).

[3] R. V. Ambartsumyan, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, Pis'ma Zh. Eksp. Teor. Fiz. 20, 597 (1974) [JETP Lett. 20, 273 (1974)]; J. L. Lyman, R. J. Jensen, J. Rink, C. P. Robinson, and S. D. Rockwood, Appl. Phys. Lett. 27, 87 (1975).

[4] S. Mukamel and J. Jortner, Chem. Phys. Lett. 40, 150 (1976), and J. Chem. Phys. 65, 5204 (1976).

[5] N. Bloembergen, Opt. Commun. 15, 416 (1975); N. Bloembergen, C. D. Cantrell, and D. M. Larsen, in *Tunable Lasers and Applications*, edited by A. Mooradian, T. Jaeger, and P. Stokseth (Springer, New York, 1976).

[6] J. G. Black, E. Yablonovitch, N. Bloembergen, and S. Mukamel, Phys. Rev. Lett. 38, 1131 (1977).

[7] M. J. Coggiola, P. A. Schulz, Y. T. Lee, and Y. R. Shen, Phys. Rev. Lett. 38, 17 (1977); E. R. Grant, P. A. Schultz, As. S. Sudbo, Y. R. Shen, and Y. T. Lee, Phys. Rev. Lett. 40, 115 (1978).

[8] J. Stone, M. F. Goodman, and D. A. Dows, J. Chem. Phys. 65, 5062 (1976).

[9] D. P. Hodgkinson and J. S. Briggs, J. Phys. B 10, 2583 (1977); C. D. Cantrell, H. W. Galbraith, and J. R. Ackerhalt, in *Multiphoton Processes*, edited by J. H. Eberly and P. Lambropolous (Wiley, New York, 1978), pp. 307-330.

[10] H. Mori, Prog. Theor. Phys. 33, 423 (1965); M. Tokuyama and H. Mori, Prog. Theor. Phys. 55, 411 (1976).

[11] S. Mukamel, I. Oppenheim, and J. Ross, Phys. Rev. A 17, 1988 (1978).

[12] C. Cohen Tannoudji, in *Cargèse Lectures in Physics*, edited by M. Levy (Gordon & Breach, New York, 1967), Vol. 2, p. 347.

[13] S. Mukamel, Chem. Phys. 31, 327 (1978).

[14] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford Univ. Press, London, 1961).

[15] M. W. Wang and G. E. Uhlenbeck, Rev. Mod. Phys. 17, 323 (1945); R. Kubo, in *Advances in Chemical Physics*, edited by I. Prigogine (Wiley, New York, 1969), Vol. 15.

[16] S. Mukamel, to be published.