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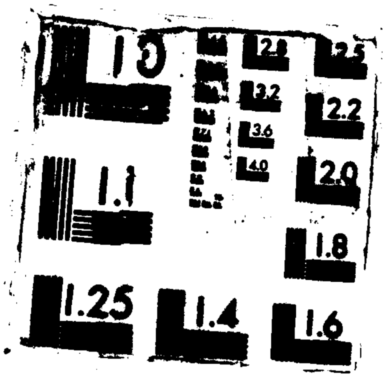
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On the Born and Markov Approximations: Phonon Relaxation and Coherent Excitation of Adsorbed Molecules

by

Sander van Smaalen and Thomas F. George

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The phonon relaxation of the vibrational adbond of an adsorbed molecule and a phonon-damped adbond irradiated by a laser are studied. In the first half of the paper, approximations are made within the Zwanzig projection operator formalism in order to arrive at a master equation for the reduced density operator of a small subsystem (the adbond) in contact with a reservoir (the phonons). The conditions of validity for the Born and Markov approximations are derived. It is shown that the master equation is only valid for times $t >> \tau$, where τ is the characteristic time of the reservoir. These results are then applied to the phonon relaxation of the vibrational adbond of physisorbed molecules. It is shown that for CO adsorbed on Ni or Cu (a strongly-bound physisorbed system), the Born and Markov approximations are not justified. For the weakly-bound system Ar on W, numerical results show that these approximations can be made. Finally, an adbond interacting with both laser radiation and lattice vibrations is considered. This system can be regarded as a subsystem (the adbond) in contact with two reservoirs, where the conditions for validity

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On the Born and Markov approximations: Phonon relaxation and coherent excitation of adsorbed molecules

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1. Introduction

In quantum mechanics, complete information about a system is contained in the wave function $|\psi\rangle$. When there is only a limited knowledge about a system, the proper way to describe its state is by the density operator,

$$\rho = \sum_{\psi} p_{\psi} |\psi\rangle\langle\psi| \tag{1}$$

where the real numbers p_{ψ} form a set of probability amplitudes,

$$\sum_{\psi} p_{\psi} = 1. \tag{2}$$

All information about the properties of a subsystem is given by the reduced density operator,

$$\sigma = \mathrm{Tr}\ \rho, \tag{3}$$

where Tr denotes the trace over all variables other than those of the subsystem.

From the Schrödinger equation, an equation for the time evolution of the density operator of a closed system is easily derived to be

$$i\hbar\frac{d\rho(t)}{dt} = [H,\rho(t)], \tag{4}$$

where H is the Hamiltonian of the system. From Eq. (4) an expression for the time derivative of the reduced density operator is obtained by taking the trace on both sides. However, this time derivative still depends on the complete density operator, because the operators Tr and H do not commute. It follows that to obtain the time evolution of $\sigma(t)$ exactly, the equation of motion for the complete density operator [Eq. (4)] need to be solved.

Often, we are interested in the properties of a very small system (e.g., one molecule) in contact with a much larger one, called the reservoir. We assume that the reservoir can be made arbitrarily large, such that there is no appreciable difference between the reduced density operator for the reservoir, $\mathrm{Tr}_s\rho$, and the density operator for the freely in time evolving reservoir, ρ_b^o. It is assumed that the latter is known. When the interaction is weak, we can try to obtain an approximate solution for the time evolution of the reduced density operator of the subsystem. If the interaction is taken into account to lowest order in perturbation theory, it is easily shown that a first-order differential equation is obtained for the reduced density operator.[1] Apart from $\sigma(t)$, it involves only the zeroth-order approximation to the reservoir density operator, ρ_b^o. For longer times, the effect of the interaction tends to build up. Therefore, there will be a time beyond which perturbation theory is not valid. To obtain an equation of motion for the subsystem reduced density operator for all times, a second approximation is necessary, usually denoted as the Markov approximation.[1]

One method for obtaining an equation of motion for the subsystem reduced density operator is the Zwanzig projection technique.[2,3] With this technique, an exact integro-differential equation for the reduced density operator of the subsystem is obtained. The two approximations necessary to arrive at a simple first-order differential equation for $\sigma(t)$ are commonly denoted as the Born approximation and the Markov approximation.[4] Recently, this method has been used to obtain the effect of the lattice vibrations of a crystal on the dynamics of an adsorbed atom.[5] In the derivation of the master equation, the Born approximation and the Markov approximation have been introduced as separate approximations.[4,5] In later studies the validity of both approximations have been studied independently.[6-11]

In this paper we shall consider the validity of both approximations from a more fundamental point of view. In Section 2 we give a review of the

Zwanzig projection operator formalism. In the next two sections the Born and Markov approximations will be introduced, and the conditions will be derived under which they are justified. It will be shown that the condition for validity is the same for both approximations. Another widely-used technique for obtaining an equation of motion for the reduced density operator of the subsystem is the so-called reservoir theory.[1,12] In Section 5 the Zwanzig projection technique will be compared with reservoir theory. In particular, the correspondence of the two approximations involved will be discussed. In Sections 6-8 we shall discuss the system of a vibrationally damped adatom and of an adatom irradiated by laser light in more detail. Numerical examples will be given based on previous experimental and theoretical work. Our conclusions are presented in Section 9.

2. Zwanzig projection operator technique

We consider a small subsystem in contact with a large reservoir. We denote the Hamiltonian of the subsystem by H_s, of the reservoir by H_b, and of their interaction by V, such that the Hamiltonian of the complete system is given by,

$$H = H_s + H_b + V. \tag{5}$$

We then define the projection operator P by,

$$P = \rho_b \, \mathrm{Tr}_b, \tag{6}$$

where ρ_b is any density operator of the reservoir and Tr_b denotes the trace over the reservoir variables. In the Zwanzig projection technique, an equation of motion for $P\rho(t)$ is derived, from which an equation of motion for the subsystem reduced density operator is directly obtained by taking Tr_b. The starting point is the equation of motion for $\rho(t)$, Eq. (4). Let L be the Liouville operator defined by,

$$L\rho = \frac{1}{\hbar}[H,\rho], \tag{7}$$

with analogous definitions for L_s, L_b, L_I and $L_o = L_s + L_b$. Then, from Eq. (4), an exact equation for $P\rho$ can be derived as[3]

$$i\frac{dP\rho(t)}{dt} = PLP\rho(t) + PL\exp[-i(1-P)Lt](1-P)\rho(0)$$
$$-i\int_0^t dt'\, PL\exp[-i(1-P)Lt'](1-P)LP\rho(t-t'). \tag{8}$$

The first term in Eq. (8) has a contribution of zeroth- and first-order in the interaction, and the last term has contributions of all orders in V. To separate the free evolution of the subsystem (determined by L_s) from the interaction with the reservoir, the following conditions are imposed on ρ_b and V:[3]

$$[\rho_b,H_s] = [\rho_b,H_b] = 0, \tag{9}$$

$$\mathrm{Tr}_b\, V\rho_b = 0. \tag{10}$$

Equation (9) puts restrictions on ρ_b, and Eq. (10) defines V and H_s for a given ρ_b. The equation of motion for $P\rho(t)$ now becomes [Eq. (8)]

$$\frac{dP\rho(t)}{dt} = \frac{1}{i\hbar}[H_s,P\rho(t)] + \frac{1}{i}PL_I\exp[-i(1-P)Lt](1-P)\rho(0)$$
$$-\int_0^t dt'\, PL_I\exp[-i(1-P)Lt'](1-P)L_IP\rho(t-t'). \tag{11}$$

The first term in Eq. (11) describes the free evolution of $P\rho(t)$, whereas the last term only gives corrections of second- and higher-order in the interaction.

To be able to estimate the contributions of the different terms, we assume that V can be written as a sum of products of a subsystem operator and a reservoir operator.[1,12] For only one term we have

$$V = R\,S. \tag{12}$$

Let us define the operator R(t) in the interaction picture by[1]

$$(R(t) = \exp[\tfrac{i}{\hbar}H_b t]\; R\; \exp[-\tfrac{i}{\hbar}H_b t]. \tag{13}$$

Furthermore, we assume that the reservoir has a characteristic time τ_c, given by

$$\mathrm{Tr}_b\{R(0)R(t)\rho_b^o\} = \mathrm{Tr}_b\{R^2(0)\rho_b^o\}\exp[-|t|/\tau_c]. \tag{14}$$

It can then be shown that the contribution of $\rho(0)$ (second term in Eq. (11)) to $P\rho(t)$ is a factor τ_c/t smaller than the contribution of the third term, if $\Delta\rho(0) = \rho(0) - \rho_b\sigma(0)$ is small. Therefore, the second term can be neglected if we are only interested in the time evolution of the subsystem for times $t \gg \tau_c$.

If $\Delta\rho(0)$ is not small, the contributions to $P\rho(t)$ can be much larger than quoted above. Requiring $\Delta\rho(0)$ to be small leads to another condition on ρ_b:

$$\rho_b \cong \mathrm{Tr}_s\rho(t). \tag{15}$$

For a large reservoir in thermal equilibrium, we can use

$$\rho_b = \rho_b^o = \frac{e^{-\beta H_b}}{\mathrm{Tr}_b e^{-\beta H_b}}. \tag{16}$$

We note that $\rho_b = \mathrm{Tr}_s\rho(0)$ is not a good choice because of Eq. (9).

3. Born approximation

The Born approximation involves the retention of only the terms of lowest order in V in Eq. (11).[4] These are obtained by replacing L by L_0 in the exponential function. The resulting equation for the subsystem reduced density operator is

$$\frac{d\sigma(t)}{dt} = \frac{1}{i\hbar}[H_s,\sigma(t)] - \mathrm{Tr}_b\int_0^t dt'\; L_I\exp[-iL_0t']L_I\rho_b\sigma(t-t'). \qquad (17)$$

In order that this be a good approximation, the term of next order in V must be much smaller than the term of second order. To test the validity of this approximation we need an estimate for the value of both terms.

We assume that, following Eq. (10), $\mathrm{Tr}_bV^3\rho_b = 0$, then the lowest-order correction to the Born approximation is of fourth order in V. That is, we need the second-order terms in the expansion of the exponential function. Neglecting the commutator of L_I with L_0, these second order terms are given by

$$+(-it')^2(1-P)L_I\exp[-i(1-P)L_0t'](1-P)L_I. \qquad (18)$$

The fourth-order contribution to $\frac{d\sigma}{dt}$ becomes

$$\left[\frac{d\sigma(t)}{dt}\right]^4 = \mathrm{Tr}_b\int_0^t dt'\; L_I\; L_I\; \exp[-iL_0t']L_I\; L_I\rho_b\sigma(t-t'). \qquad (19)$$

Use of Eqs. (12) - (14) shows that the integrand involves a reservoir correlation function $\mathrm{Tr}_b\{R^2(0)R^2(-t\cdot)\}$, which is approximately

$$\mathrm{Tr}_b\{\rho_bR^2(0)R^2(-t')\} \cong [\mathrm{Tr}_b\{\rho_bR^2\}]^2\exp[-|t'|/\tau_c]. \qquad (20)$$

The order of magnitude of the subsystem factor in the integrand is given by

$$\mathrm{Tr}_s\{S^4\sigma(0)\}e^{i\omega_0t'} \cong [\mathrm{Tr}_s\{S^2\sigma(0)\}]^2e^{i\omega_0t'}, \qquad (21)$$

where ω_0 is a typical transition frequency of the subsystem. Given the definition

$$v^2 = \mathrm{Tr}_b\{\rho_bR^2\}\mathrm{Tr}_s\{\sigma(0)S^2\}, \qquad (22)$$

the integral of Eq. (19) can be evaluated by using these approximations to yield

$$\left[\frac{d\sigma(t)}{dt}\right]^{(4)} = \frac{v^4\tau_c^3}{\hbar^4}\,\rho_b\sigma(t). \qquad (23)$$

Hereby is the upperbound of the integral extended from t to infinity, which because of Eq. (20) introduces an error of the order $(\frac{\tau_c}{t})$, which is comparable to the error introduced by neglecting the contribution of $\rho(0)$. The effect of the factor $e^{i\omega_0 t'}$ in Eq. (21) is to single out the Fourier terms in the expansion of the correlation function with $\omega = \omega_0$. An analogous calculation for the second-order term gives[12]

$$\left[\frac{d\sigma(t)}{dt}\right]^{(2)} = \frac{v^2\tau_c}{\hbar^2}\,\rho_b\sigma(t). \qquad (24)$$

For the Born approximation to be valid we have the condition

$$\gamma^{(4)} \ll \gamma^{(2)}, \qquad (25)$$

where $\gamma^{(n)}$ is the n-th-order contribution in the interaction to the relaxation constant, γ. The latter is defined as a typical matrix element of the Liouville operator describing the time evolution of $\sigma(t)$ due to the interaction with the reservoir (second term in Eq. (17)). Substitution of Eqs. (23) and (24) into (25) gives

$$\frac{v^2\tau_c^2}{\hbar^2} \ll 1. \qquad (26)$$

4. Markov approximation

Equation (11) shows that the time-derivative of $\sigma(t)$ depends on the value of $\sigma(t)$ on previous times. In the Markov approximation this integro-differential equation is replaced by a simple first-order differential equation for $\sigma(t)$. From Eq. (11) it follows that $\sigma(t)$ is a fast-oscillating function, due to the free evolution of the subsystem. These rapid oscillations can be eliminated by transformation to the interaction picture,[1]

$$\tilde{\sigma}(t) = \exp[\tfrac{i}{\hbar}H_s t]\ \sigma(t)\ \exp[-\tfrac{i}{\hbar}H_s t]. \tag{27}$$

The equation of motion for $\tilde{\sigma}(t)$ is [Eq. (11)]

$$\frac{d\tilde{\sigma}(t)}{dt} = -\exp[\tfrac{i}{\hbar}H_s t]\mathrm{Tr}_b\int_0^t dt'\ \{L_I\exp[-i(1-P)Lt'](1-P)L_I\rho_b\exp[-\tfrac{i}{\hbar}H_s(t-t')]$$

$$\tilde{\sigma}(t-t')\exp[\tfrac{i}{\hbar}H_s(t-t')]\}\exp[-\tfrac{i}{\hbar}H_s t]. \tag{28}$$

In the previous section it was derived that the integrand involves a factor $\exp[-|t'|/\tau_c]$. Therefore, if $\tilde{\sigma}(t)$ does not change much on a time scale of the order τ_c, $\tilde{\sigma}(t-t')$ may be replaced by $\tilde{\sigma}(t)$ in the integrand. The temporal changes in $\tilde{\sigma}(t)$ are of the order $\gamma.\Delta t$, so that we obtain as the condition for the validity of the Markov approximation

$$\gamma \ll \tau_c^{-1}. \tag{29}$$

γ is already approximately evaluated in the previous section [Eq. (24)]. The condition under which the Markov approximation is justified then becomes

$$\frac{V^2\tau_c^2}{\hbar^2} \ll 1. \tag{30}$$

Comparison of Eq. (26) and Eq. (30) shows that the conditions for validity of the Born approximation and of the Markov approximation are the same. A similar result was obtained by Fano[13] in his treatment of pressure broadening.

Within the Born and Markov approximations, the equation of motion for the reduced density operator of the subsystem is

$$\frac{d\sigma(t)}{dt} = \frac{1}{i\hbar}[H_s,\sigma(t)] - \Gamma\sigma(t), \tag{31}$$

where Γ is the Liouville operator describing relaxation

$$\Gamma = \mathrm{Tr}_b \int_0^\infty dt' \, L_I \exp[-iL_0 t'] L_I \rho_b \exp[iL_S t']. \tag{32}$$

Substitution of the solution of Eq. (31) into Eq. (11) shows that the Markov approximation also involves the neglect of terms of fourth and higher order in V.

The steady state (or equilibrium) for the subsystem requires special consideration. That such a state actually exists is, for example, discussed by Van Hove.[14] It is characterized by $\tilde{\sigma}(t) = \tilde{\sigma}(\infty)$ being independent of time. It follows immediately that the Markov approximation can be made without any error. Noting that $\frac{d\tilde{\sigma}(t)}{dt} = 0$ for any strength of the interaction then leads to the conclusion that the contribution to Eq. (28) of the terms for each power of V should be zero independently. Therefore, the steady-state solution can correctly be obtained from the expression within the Born and Markov approximations [Eq. (31)], even if the Born and Markov approximations are not valid otherwise. Note that then the relaxation constants [Eq. (32)] do not correctly describe the time evolution to equilibrium, however close the initial state and the steady state might be.

5. Comparison with reservoir theory

An alternative procedure for obtaining an approximate expression for $\sigma(t)$ is reservoir theory.[1,12] The starting point is the equation of motion for the complete density operator [eq. (4)] in the interaction picture,

$$\frac{d\tilde{\rho}(t)}{dt} = \frac{1}{i\hbar}[\tilde{V}(t),\tilde{\rho}(t)], \tag{33}$$

where $\tilde{V}(t)$ and $\tilde{\rho}(t)$ are defined analogously to Eqs. (13) and (27). Substitution of the formal solution of Eq. (33) on the right-hand side and a change of variables in the integral gives

$$\frac{d\tilde{\rho}(t)}{dt} = (\frac{1}{i\hbar})[\tilde{V}(t),\tilde{\rho}(0)] + (\frac{1}{i\hbar})^2\int_0^t dt' \, [\tilde{V}(t),[\tilde{V}(t-t'),\tilde{\rho}(t-t')]]. \qquad (34)$$

An expression for the time derivative of $\tilde{\sigma}(t)$ can be obtained by taking Tr_b on both sides in Eq. (34), although it still depends on the complete density operator $\tilde{\rho}(t)$.

Equation (34) is exact, and comparison of this equation with the expression obtained with the Zwanzig projection technique [Eq. (11)] shows that both involve a term depending on the initial time density operator. In reservoir theory there is a term of apparently second order in the interaction, and dependent on the complete density operator. This term corresponds to the third term in Eq. (11), the latter which includes contributions of all orders in V, but involves only the subsystem reduced density operator. Apparently the contributions of higher order in V are contained in the coherences between the subsystem and the reservoir, still present in Eq. (34). The first approximation to be made is therefore the factorization of $\tilde{\rho}(t)$,

$$\tilde{\rho}(t) = \rho_b\tilde{\sigma}(t) + \Delta\tilde{\rho}(t), \qquad (35)$$

where again the conditions of Eqs. (9), (10) and (15) are imposed on ρ_b and $\tilde{V}$. Substituting Eq. (35) into (34) and discarding all terms involving $\Delta\tilde{\rho}(t)$, we obtain expression which is identical to Eq. (17). That is, the factorization of $\tilde{\rho}(t)$ in reservoir theory corresponds to the Born approximation in the Zwanzig projection technique. Indeed, it can be shown that the conditions for validity for both approximations are the same.[12] Then, the Markov approximation (replacement of $\tilde{\sigma}(t-t')$ by $\tilde{\sigma}(t)$) is also the same in both approaches. As in the Zwanzig projection technique, the factorization of $\bar{\rho}(0)$ in the first term [Eq. (34)] introduces an error of order V^2, but a factor $\frac{\tau_c}{t}$ smaller than the second term.[15,16] The factorization of $\bar{\rho}(t-t')$ in the second term introduces an error of order V^4. Therefore, the neglect of $\Delta\rho(0)$ is an essentially different approximation than the factorization of $\bar{\rho}(t-t')$.

As shown in Sections 2-4, the term involving $\rho(0)$ and the error introduced by the extension of the integral from t to infinity are of the same order in V as the relaxation constant, but are smaller by a factor τ_c/t. Therefore, the equation of motion for $\bar{\sigma}(t)$, derived within the Born and Markov approximations [Eq. (31)], is only valid for times $t \gg \tau_c$. Since the condition for validity of the Born and Markov approximations [Eqs. (26) and (30)] requires the relaxation time of the subsystem to be much larger than the correlation time of the reservoir, this time interval still includes most of the transient regime before the subsystem reaches the steady state.

Disregarding, for the moment, the matrix character of the equation of motion for $\bar{\sigma}(t)$ [Eq.(31)], the solution for $\bar{\sigma}(t)$ is ($\tau_c \ll t \ll \Upsilon^{-1}$)

$$\bar{\sigma}(t) = \pm(\Upsilon t + \Upsilon t\ O(\frac{\tau_c}{t}))\bar{\sigma}(0), \tag{36}$$

where the terms of $O(\frac{\tau_c}{t})$ represent the neglected contributions of $\bar{\rho}(0)$ and the extension of the integral. The prefactor of this term is essentially of the same order of magnitude as the relaxation constant itself. Equation (36) shows that the relative error in the value of $\bar{\sigma}(t)$ is of the order τ_c/t. However, the relative error in the different $\bar{\sigma}(t+\tau_c) - \bar{\sigma}(t)$ is only of the order $(\tau_c/t)^2$. Since the value of this difference is of the order τ_c/t, it follows that Eq. (31) describes the variation of $\bar{\sigma}(t)$ on any time scale with the same relative accuracy as the absolute value of $\bar{\sigma}(t)$ is known. Therefore, the so-called coarse-grained averaging is not necessary.[1,12,15,16]

6. Phonon relaxation of an adsorbed molecule

Thermal desorption and laser-induced desorption have been the subjects of many studies.[5-8,17-21] The model employed by many authors for the vibrationally bounded molecule is that of a one-dimensional oscillator.[5,9,20,21] Only motions of the molecule perpendicular to the surface are taken into account. This approach assumes that the effects of (frustrated) rotations of the molecule on the substrate can be neglected. Although we cannot give a rigorous proof for the correctness of this assumption, there are some experiments which support it. For example, for CO on copper, it was shown that CO adsorbs in an on-top conformation, with a relatively small angle (~ 10 deg.) for the amplitude of the rotational vibration mode.[22]

The interaction between the admolecule and the substrate is usually described by a Morse potential, which gives a fair description of the adsorbate-substrate potential. It also has the feature that the eigenvalues and eigenstates can be obtained analytically, thus simplyfying the further analysis. The discrete levels are identified with bound states of the adsorbate, and the continuum levels correspond to gaseous molecules. Desorption is described by a transition from a bound state to a continuum state.[5]

One interesting problem, which is also experimentally accessible, is the calculation of the linewidth of the vibrational adbond due to the interaction with the lattice vibrations of the substrate. We denote the Morse potential by $V_m(z-z_0)$, with z the distance of the admolecule above the surface when the lattice vibrations are absent. The proper definition of the interaction Hamiltonian between the adbond vibration (subsystem) and the lattice vibrations (reservoir), in accordance with Eq. (10), is[5]

$$V(z-z_o-u_z) = V_m(z-z_o-u_z) - \langle V_m(z-z_o-u_z)\rangle, \qquad (37)$$

where $\langle \ldots \rangle = \mathrm{Tr}_p(\rho_b^o \ldots)$ denotes the average over the phonons, and $u_z = u_z(t)$ is the z-component of the temporal vibration amplitude of the surface atom due to the lattice vibrations. The subsystem Hamiltonian is

$$H_s = T + \langle V_m(z-z_o-u_z)\rangle, \qquad (38)$$

where T denotes the kinetic energy of the admolecule. The averaged potential $\langle V(z-z_o-u_z)\rangle$ is again a Morse potential, but with renormalized values for its depth and equilibrium distance, z_o.[5] By using Eq. (37), the relaxation constants for the adbond reduced density operator can be obtained within the Born and Markov approximations in a straightforward calculation.[5] In the resulting expression, the reservoir is represented by the occurrence of only the displacement autocorrelation function $\langle u_z(t)u_z(o)\rangle$.

To test the applicability of the Born and Markov approximations, we can use Eqs. (26), (29), and (30), which give as the condition for validity

$$\gamma\tau_p \ll 1. \qquad (39)$$

The characteristic time of the displacement autocorrelation function, τ_p, can be identified with half the phonon lifetime. For metals, experimental determinations yield quantities of the order 10^{-12}s.[23,24] An experimental determination of the linewidth ($\sim\gamma$) is available for the $0 \rightarrow 1$ transition of the Ni...C vibrational mode of CO adsorbed on a Ni(100) surface. A value of 15cm^{-1} $\sim$ 2.8 10^{12} s^{-1} is found.[25] Then

$$\gamma\tau_p = 1.4, \qquad (40)$$

which is of the order one. It follows that for this system the Born and Markov approximation are questionable, at best.

The estimate mentioned above is obtained by considering phonons only (i.e., the phonon life time is used). It was shown by Persson and Persson[26] that for metallic substrates a damping involving a coupling of the vibrational mode with the conduction electrons will be much larger than the phonon damping. The strength of the coupling between the vibrational adbond mode and the electronic degrees of freedom is, amongst others, dependent on the derivative of the adparticle M.O. energy with respect to the vibration coordinate. For the weak ad-bonds, as are considered here, this derivative will be much smaller than for the internal vibration considered by Persson and Persson.[25] Also, the phonon damping will be much stronger for the low-frequency adbond than for the internal mode. Therefore, we believe that, relative to the electron-loss mechanism, the phonon-damping will have a much larger contribution to the linewidth than in the case of internal vibrations of a molecule on a metallic substrate.

Theoretical calculations of the relaxation constants, performed within the Born and Markov approximations, have been published by Hood et al.[27] and Volokitin et al.[28] For CO absorbed on Cu, a system similar to CO on Ni, a value of $3.1\ 10^{13}\ s^{-1}$ was obtained for the $0 \rightarrow 1$ transition at $T = 300$ K.[27] In this calculation a Debye spectrum was used for the phonon dispersion relation. For CO adsorbed on Ni, a value of $\gamma = 1.4\ 10^{13}\ s^{-1}$ was obtained, also using a Debye spectrum and at $T = 300$ K.[28] With $\tau_p = 5\ 10^{-13}$ s, we obtain $\gamma\tau_p > 1$, and it follows that the Born and Markov approximations are not justified within the model systems employed by those authors. The values for γ quoted above are obtained for an infinite phonon lifetime. The effect of a finite phonon lifetime is to enlarge the calculated γ by at least a factor ten.[27] (A value $\tau_p = 10^{-12}$ s was used in those calculations.) The Born and Markov approximations are then even more questionable.

Using a more realistic surface phonon spectrum due to Black[29], it was possible to reproduce the experimental value for the Ni...C vibration very well ($\gamma = 13.3$ cm^{-1}).[28] However, an infinite phonon lifetime was used. Since a finite lifetime effectively broadens the phonon spectrum, and since the spectrum used is sharply peaked[29], it is to be expected that inclusion of a finite lifetime will give an even more dramatic increase of γ than for the Debye spectrum. Again, a much larger value than experiment will be obtained. The conclusion is that the Born and Markov approximations are not justified for this system.

CO adsorbed on Ni or Cu is an example of a strongly-bound physisorbed system. For the weakly-bound physisorbed system Ar on W, a value of $\gamma = 6\times10^{11}$ s was obtained at T = 30 K and using a Debye spectrum.[27] (Note that T = 30 K for Ar and T = 300 K for CO both correspond to the situation $k_B T \lesssim \frac{1}{2}\hbar\omega_0$, where ω_0 is the fundamental vibration frequency.) Now $\gamma\tau_p = 0.3$, and the Born and Markov approximation might be valid, especially since a more realistic surface phonon dispersion relation is expected to reduce the calculated value of γ considerably. Because the fundamental vibration frequency is smaller than the Debye frequency, the inclusion of a finite τ_p in the calculation of γ hardly affects the result.[27]

7. Multiphonon processes

The interaction potential between the admolecule and the substrate can be expanded in a power series in u_z,

$$V_m(z-z_o-u_z) = V_m(z-z_o) - \frac{\partial V_m(z-z_o)}{\partial z}u_z + \frac{1}{2}\,\frac{\partial^2 V_m(z-z_o)}{\partial z^2}u_z^2 + \ldots, \qquad (41)$$

which shows that the interaction Hamiltonian can indeed be written as a sum of products of a subsystem and a reservoir operator. The latter are identified with the various powers of u_z. The subsystem operators are the derivatives of the adbond potential. $V_m(z-z_0)$ is included in the subsystem Hamiltonian. The term proportional to u_z^n gives rise to n-phonon processes, i.e., a transition between levels of the adbond is accompanied by the emission and/or absorption of n phonons. It can be shown that, for a Morse potential, the contribution of n-phonon processes to the relaxation constant is exactly given by terms involving $\langle u_z(t)u_z(0)\rangle^n$ in the expression for γ obtained by using the full potential of Eq. (37).[30] For a system in which the fundamental vibration frequency is larger than the Debye frequency (e.g., CO on Ni or Cu), the multiphonon processes give an important contribution to the relaxation constant.[6,27,30]

It has been argued that when multiphonon processes in second-order perturbation theory give a significant contribution, higher orders in the interaction also need to be included.[6,7,8] That this is not the case already follows from the fact that the conditions for validity of the Born and Markov approximations [Eqs. (26) and (30)] are obtained without any assumption for the form of the interaction potential. Explicitly, the multiphonon contributions to γ are given by [Eq. (24)]

$$\gamma_n^{(2)} = \frac{v_n^2 \tau_p}{\hbar^2} \tag{42}$$

in second-order perturbation theory. In fourth-order of the interaction they are [Eq. (23)]

$$\gamma_n^{(4)} = \frac{v_n^4 \tau_p^3}{\hbar^4} \tag{43}$$

where v_n defines the contribution of n-phonon processes to the relaxation constant. For n=1, 2 it is given by

$$v_1 = \mathrm{Tr}_{p+s}\,\{\rho_b\sigma(0)u_z^2(\frac{\partial V_m(z-z_o)}{\partial z})^2\} \tag{44}$$

$$v_2 = \mathrm{Tr}_{p+s}\,\{\rho_b\sigma(0)u_z^4(\frac{\partial V_m(z-z_o)}{\partial z^2})^2\} \tag{45}$$

with similar expressions for the higher values of n. The relative importance of each of the multiphonon processes follows from the ratio of the corresponding $\gamma_n^{(2)}$, i.e., it is determined by v_n^2/v_m^2. However, the contribution of higher orders in perturbation theory is determined by the smallness of the parameters $v_n^2\tau_c^2/\hbar^2$. More precise, they can always be neglected if [Eq. (26)]

$$\frac{(\sum_n v_n^2)\tau_c^2}{\hbar^2} << 1, \tag{46}$$

where the summation runs over all the multiphonon contributions. The conclusion is that the incorporation of multiphonon processes within second-order perturbation is a valid procedure, only as long as the Born and Markov approximations are justified [Eqs. (26), (30) and (46)].

The fact that Gortel et al.[6] find an appreciable contribution of the fourth-order terms merely indicates that the Born and Markov approximation cannot be made. It then is questionable that terms of up to fourth order in the interaction are sufficient to calculate γ accurately. Moreover, the fourth-order correction as obtained by Gortel et al.[6,7,8], or as given by Eq. (43), only includes the terms connected with the Born approximation. Additional correction terms of fourth order in V arise due to the Markov approximation not being valid anymore.

8. Coherent excitation of an adsorbed molecule

An adsorbed molecule irradiated by laser light is a widely studied system.[17] Examples of processes studied are laser-induced surface chemical reactions and laser-induced desorption. The effect of the laser is to directly excite the vibrational adbond mode or an internal mode of the adspecies. Subsequently, relaxation occurs through the interaction with the lattice vibrations, as is described in previous sections.

The system can now be considered as a subsystem (the adbond) in contact with two reservoirs (the phonons and the laser, respectively). Within the Born and Markov approximations, a master equation is obtained, with relaxation constants given as the sum of a phonon part and a term due to the laser-admolecule interaction,

$$\gamma = \gamma_p + \gamma_r . \qquad (47)$$

The expression for γ_p is identical to the one obtained for the adbond with the phonons only [Eq. (32)]. The laser part, γ_r, can be obtained in an analogous calculation, employing the laser-adbond interaction as perturbation.[20]

By an analysis analogously to Section 3, it can be shown that the condition for validity of the Born approximation is the same as if each reservoir is considered independently, we obtain,

$$\gamma_p \tau_p << 1, \qquad (48a)$$

$$\gamma_r \tau_r << 1. \qquad (48b)$$

However, the condition for validity of the Markov approximation is different. It is given by [Eq. (29)]:

$$\gamma_p \tau_r << 1, \qquad (49a)$$

$$\gamma_r \tau_r << 1. \qquad (49b)$$

That is, the change of $\bar{\sigma}(t)$ is required to be small on a timescale of the longest correlation time, τ_r. It follows that the conditions for validity of the Born and Markov approximations are not the same, as was seen to be the case when only one reservoir is present (Sections 3 and 4). Generally, they are more restrictive for the Markov approximation than for the Born approximation.

Dependent on the relative strength of the laser adbond and phonon adbond intereaction, the conditions Eqs. (48) and (49) can be simplified. A number of limiting cases are given in Table 1. In Section 6 it was shown that for actual systems $\gamma_p\tau_p$ is more or less of the order one. Since $\tau_r >> \tau_p$, it follows that the conditions for validity [Eqs. (48) and (49) and Table 1] can not be matched, except in the case of a weak laser: $\gamma_r < (\frac{\tau_p}{\tau_r})\gamma_b$. Table 1 shows that the condition for validity of the Markov approximation is the most restrictive one. It is only in this case, with $\gamma_p\tau_p << 1$ but $\gamma_p\tau_r << 1$, that the generalized master equation derived by Beri et al.[10] and Peremans et al.[11] applies. However, the numerical examples given by these authors refer to laser intensities stronger than allowed by Table 1. It is interesting to note that the Markov approximation does not become better when the laser power is reduced further. The relative error in γ remains of the order $\gamma_p\tau_r$. This is easily understood if we realize that the Markov approximation requires $\bar{\sigma}(t)$ to have only a small change on a time τ_r. This change is determined by both the phonons and the laser [Eq. (47)]. If $\gamma_r << \gamma_p$, then the laser has relatively little effect on the changes induced in $\bar{\sigma}(t)$.

A situation of great experimental interest is when we start with an adbond in equilibrium with the phonons, and then turn on the laser. This is, for example, encountered in spectroscopy. The condition under which the

Born approximation is justified is again given by Eq. (48). However, the condition for validity of the Markov approximation is different now. Initially, there is no change in $\delta(t)$ due to the phonons. When the laser is turned on, an upper limit for the change in $\delta(t)$ over a time interval t is given by γ_r t. The actual change will be smaller because the phonon interaction forces $\delta(t)$ into the direction of equilibrium. The condition for validity of the Markov approximation then becomes

$$\gamma_r \tau_r \ll 1, \tag{50}$$

instead of Eq. (49). It follows that for weak lasers, $\gamma_r < (\frac{\tau_p}{\tau_r})\gamma_b$, the condition for validity of the Born and Markov approximations is the same as if each reservoir could be considered independently.

Finally, we want to discuss the situation where the Born and Markov approximations are made with respect to one reservoir only, e.g., the phonons. For laser intensities which lead to a change in $\delta(t)$ smaller than the change induced by the phonons, the conditions under which the Born and Markov approximations are justified are the same as in the absence of the laser [Eq. (30)]. However, if the rate of change of $\delta(t)$ due to the laser is larger than the due to the phonons, the Markov approximation is only justified if the change in $\delta(t)$ in a time τ_p due to the laser is small.

9. Conclusions

The conditions under which the Born and Markov approximations can be made within the Zwanzig projection formalism have been analyzed. It is shown that the condition for validity of both approximations is the same. A comparison with reservoir theory is made, and it is pointed out that the Born approximation in the Zwanzig projection technique corresponds to the factorization of the density operator in reservoir theory.

Apart from the Born and Markov approximations, the derivation of a master equation [Eq. (31)] relies on two other approximations: extension of the upper bound of the integral over time from finite t to infinity, and the factorization of the initial time density operator. Both approximations introduce errors in the relaxation constant of the order τ_c/t, but which are of the same order in the interaction. Therefore, the approximate equations apply only for times $t \gg \tau_c$.

For $t \ll \gamma^{-1}$, the value of $\partial(t)$ is proportional to γt, with an error due to the initial time factorization of the order $\gamma \tau_c$. On a time scale τ_c, $\partial(t)$ changes by an amount $\gamma \tau_c$; however, the error changes only by an amount of the order $(\frac{\tau_c}{t})\gamma\tau_c \ll \gamma\tau_c$. Therefore, the details of the time evolution of $\partial(t)$ are preserved on any time scale, although its absolute value is only known with an error of the order $\gamma \tau_c$. This conclusion contradicts the idea of a coarse-grained average,[1,12,15,16] and indeed in the derivation presented here a coarse-grained averaging procedure was not necessary.

The results of Sections 3-5 are applied to the case of phonon relaxation of the vibrational levels of an adatom. It is found that for CO adsorbed on Ni or Cu (an example of a strongly-bound physisorbed system), the Born and Markov approximation are not justified. For W on Cu (an example of a weakly-bound physisorbed system), it is shown that the Born and Markov approximation can be made.

In Sections 6-8 the interaction of laser radiation with a phonon-damped vibrational adbond is discussed. This system can be seen as a small subsystem (the adbond) in contact with two reservoirs. It is shown that the conditions for validity of the Born and Markov approximations are different from each other, and in fact, for the Markov approximation, more restrictive than in the case with a single reservoir [Eqs. (48) and (49)]. For a weak laser, i.e., one with much less exciting power than the relaxation power of the phonons, the condition for validity of the Born approximation is (Table 1)

$$\gamma_b \tau_b \ll 1, \tag{51}$$

and the condition for validity of the Markov approximation is

$$\gamma_b \tau_r \ll 1. \tag{52}$$

It follows that there is a region of strength of phonon interaction where the Born approximation can be made, but the Markov approximation not. Then, a generalized master equation should be used to describe the time evolution of $\bar{\sigma}(t)$.[10,11] However, for an initial condition where the adbond is in equilibrium with the phonons, the equation for validity of the Markov approximation [Eq. (52)] reduces to $\gamma_b \tau_b$, i.e., the same as Eq. (51). It follows that for analysis of spectroscopic data, the Born and Markov approximations are justified if the reservoir-subsystem interaction obeys Eq. (51). However, when spectroscopy is used in non-equilibrium situations (e.g., to follow the course of a chemical reaction), the reservoir-subsystem interaction has to obey the much more severe condition of Eq. (52). For phonon relaxation this can hardly be expected to be the case.

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Table 1. Conditions for validity of the Born and Markov approximations for various ratios of the strength of the laser and phonon interactions.

Ratio of relaxation constants	Born approximation	Markov approximation
$\gamma_r < (\frac{\tau_p}{\tau_r})\gamma_p$	$\gamma_p\tau_p << 1$	$\gamma_p\tau_r << 1$
$\gamma_r = \gamma_p$	$\gamma_p\tau_r << 1$	$\gamma_p\tau_r << 1$
$\gamma_r > \gamma_p$	$\gamma_r\tau_r << 1$	$\gamma_r\tau_r << 1$

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