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Inelastic electron tunneling through a vibrational modulated barrier in STM

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Abstract: *Using a many body formalism, we have studied the effect of the modulation of the tunneling barrier by the vibrating molecule, on the inelastic tunneling current in STM. In our model, the dominant inelastic term appears in the first order of the perturbation theory. We have considered also the second and the third order elastic and inelastic terms, which can contribute to the tunneling current in the STM.*

Key words: Scanning Tunneling Microscopy, elastic and inelastic tunneling

Recent experiments proved the possibility to perform inelastic electron tunneling with STM, through vibrating molecules [1,2]. Previous theories of inelastic electron tunneling, model this process by dipole coupling [3,4], or tunneling through an adsorbate resonance [5-7]. Detailed microscopic calculations based on Green Function technique [8] or Density Functional Theory [9], explain the selection rules observed in experiments, by destructive interferences of inelastic scattering processes.

In the present paper, we model the inelastic tunneling of electrons using a similar Hamiltonian as used by Persson and Baratoff [5]. We consider that the vibration of the molecule modulates the tunneling barrier and that the coupling of the tunneling electrons to this vibration is the main perturbation.

We model the following physical process: electrons tunnel from an electron resonance localized on the STM tip to an electronic resonance of a vibrating molecule absorbed on a metallic surface (Fig.1). The corresponding projected densities of states on the states ε_B and ε_A are denoted $\rho_B(\varepsilon)$ and $\rho_A(\varepsilon)$.

The process is modeled by the Hamiltonian:

$$H = \varepsilon_A C_A^+ C_A + \sum_{k_R} \varepsilon_{k_R} a_{k_R}^+ a_{k_R} + \sum_{k_R} \left(V_{Ak_R} a_{k_R}^+ C_A + H \cdot C\right) + \varepsilon_B C_B^+ C_B + \sum_{k_L} a_{k_L} a_{k_L}^+ + \\ + \sum_{k_L} \left(V_{Bk_L} a_{k_L}^+ C_B + H \cdot C\right) + \hbar\Omega \upsilon^+ \upsilon + T_{AB}(Q)\left(C_A^+ C_B + C_B^+ C_A\right) \tag{1}$$

- $\varepsilon_A, \varepsilon_B$ – are the electronic levels close to the Fermi levels of the substate and the tip;
- $\varepsilon_{k_L}, \varepsilon_{k_R}$ - label the energy levels of the one particle eigenstates of the tip (L) and the substrate (R);
- V_{Bk_L}, V_{Ak_L} are the matrix elements for the electron transfer between the tip and ε_B level, and between the substrate and ε_A level;
- $\hbar\Omega$ - is the vibration energy of the adsorbate;
- $C_A^+, C_A, C_B^+, C_B, a_{k_L}^+, a_{k_L}, a_{k_R}^+, a_{k_R}, \upsilon^+, \upsilon$ are the annihilation and creation operators for the $\varepsilon_A, \varepsilon_B, \varepsilon_{k_L}, \hbar\Omega$ states respectively;
- Q is the displacement corresponding to the vibration mode of the adsorbate.

We neglect the dependence of ε_A and ε_B on Q, but we consider the dependence of T_{AB} on Q $\left(T_{AB}(Q)\right)$. T_{AB} is directly related to the STM barrier and is modulated by the vibration of the molecule.

By expanding T_{AB} to first order in Q we have:

$$T_{AB}(Q) = T_{AB}^{\theta}(O) + \left.\frac{\partial T_{AB}}{\partial Q}\right|_{O=0} Q = T_{AB}^0 + T_{AB}^1\left(\upsilon + \upsilon^+\right) \tag{2}$$

The Hamiltonian (1) can be rewritten using (2):

$$H = H_0 + T_{AB}^0\left(C_A^+ C_B + C_B^+ C_A\right) + T_{AB}^1\left(C_A^+ C_B + C_B^+ C_A\right)\left(\upsilon + \upsilon^+\right) \tag{3}$$

H_0 is the quadratic part of the Hamiltonian, and can be diagonalized as in [5]. After the diagonalization we obtain:

$$\begin{aligned}
&H = H_0 + V \\
&H_0 = \sum_{\alpha} \varepsilon_\alpha C_\alpha^+ C_\alpha + \sum_{\alpha} \varepsilon_\beta C_\beta^+ C_\beta + \hbar\Omega \upsilon^+ \upsilon \\
&V = V_1 + V_2 \\
&V_1 = T_{AB}^0 \sum_{\alpha_1\beta_1} \left(<b|\beta_1><\alpha_1|a> C_{\alpha_1}^+ C_{\beta_1} + H \cdot C \right) \\
&V_2 = T_{AB}^1 \left(\upsilon + \upsilon^+ \right) \sum_{\alpha_2\beta_2} \left(<b|\beta_2><\alpha_2|a> C_{\alpha_2}^+ C_{\beta_2} + H \cdot C \right)
\end{aligned} \tag{4}$$

$\{|\alpha_i>\}$, $\{|\beta_i>\}$ denote the one particle electronic states of the adsorbate-substrate system, and of the tip. The projected densities of states on ε_A and ε_B states are defined:

$$\begin{aligned}
\rho_A(\varepsilon) &= \sum_{\alpha} |<a|\alpha>|^2 \delta(\varepsilon - \varepsilon_\alpha) \\
\rho_B(\varepsilon) &= \sum_{\beta} |<b|\beta>|^2 \delta(\varepsilon - \varepsilon_\beta)
\end{aligned} \tag{5}$$

Let us consider the next expansion of the transition operator:

$$T = V + V \frac{1}{\varepsilon - H_0 + I_0} V + V \frac{1}{\varepsilon - H_0 + I_0} V \frac{1}{\varepsilon - H_0 - I_0} V + \cdots \tag{6}$$

We evaluate the transition matrix elements in the first, second and third order between the next initial and final states:

$$\begin{aligned}
&|in> = |1_{\chi_0} 0_{\beta_{1i}} 1_{\beta_{2i}}; 0_{\alpha_0} 0_{\alpha_{1i}} 1_{\alpha_{2i}} n_{iph}> \\
&|fin> = |0_{\beta_0} 0_{\beta_{1i}} 1_{\beta_{2i}}; 1_{\alpha_0} 0_{\alpha_{1i}} 1_{\alpha_{2i}} n_{fph}>
\end{aligned} \tag{7}$$

- 1_α denotes the occupation of the state α with one electron;
- 0_α denotes the empty α state;

- $|\alpha_{1i}>, |\alpha_{2i}>$ are intermediate states up (below) the Fermi level;
- $n_{i,ph}, n_{f,ph}$ indicate the number of phonons in the initial (final) state.

For elastic transition $n_{i,ph} = n_{f,ph} = 0$. For inelastic transition with emission of one phonon $n_{i,ph} = 0, n_{f,ph} = 1$, etc...The above $|in>$ and $|fin>$ states correspond to transition (elastic or inelastic) for one state electron. It is very easy to extend the notation, considering two (or more) electrons processes.

In the first order of the development (6) we have elastic processes and inelastic processes with one electron indicated symbolically in Fig.2. The matrix elements corresponding to these processes are:

$$\begin{aligned} T^{(1)}_{elastic} &= < fin_e|V_1 + V_2|in> = T^0_{AB} < b|\beta_0 >< \alpha_0|a> \\ T^{(1)}_{inelastic} &= < fin_i|V_1 + V_2| > = T^1_{AB} < b|\beta_0 >< \alpha_0|a> \end{aligned} \qquad (8)$$

All the matrix elements (elastic or inelastic) in the second order involving one-electron processes vanish. In fact, this statement is valid for all nth order matrix elements with even n (n≥2). This is not valid in Persson and Baratoff model in which the first nonvanishing inelastic processes with one tunneling electron are in the second order. The explanation of this fact is due to the presence of the coupling between the resonant level and the vibration mode in Persson and Baratoff model. This coupling term is not included in our model.

The matrix elements in the second order are:

$$T_{ij} = < fin\left|V_i \frac{1}{\varepsilon - H_0 + i_0} V_j\right|in>, \text{ with } i, j = 1,2 \qquad (9)$$

The nonvanishing matrix elements in the second order involve two electrons. The elastic and inelastic processes in the second order are presented in Fig.3.

The matrix elements in the third order are:

$$T_{ijk} = < fin\left|V_i \frac{1}{\varepsilon - H_0 + i_0} V_j \frac{1}{\varepsilon - H_0 + i_0} V_k\right| in >, \text{ with } i, j, k = 1,2 \quad (10)$$

The matrix elements in the third order involve one or three electron processes. These processes can be elastic processes or inelastic processes with one, two or three phonons (Fig.4). All the two electron processes in the third order vanish. Other nonvanishing matrix elements in the third order are inelastic processes with emission of one, two or three phonons, but the electronic events are the same as in Fig.4, a$\div$d.

Now we evaluate the tunneling currents corresponding to the first order terms indicated in Fig.2. For the elastic tunneling current we have:

$$I^{(1)}_{elastic} = \sum_{\alpha_0\beta_0} T^{(1)}_{elastic}\Theta\left(\varepsilon_F - \varepsilon_{\beta_0}\right)\left[1 - \Theta\left(\varepsilon_F - eV - \varepsilon_{\alpha_0}\right)\right]\delta\left(\varepsilon_{\alpha_0} - \varepsilon_{\beta_0}\right) \quad (11)$$

where $\Theta\left(\varepsilon_F - \varepsilon_{\beta_0}\right)$ is the Fermi Dirac distribution at zero temperature.

The corresponding elastic conductance is:

$$\begin{aligned}\frac{\partial I^{(1)}_{elastic}}{\partial V} &\approx \frac{4\pi e^2}{\hbar}\left|T^0_{AB}\right|^2 \sum_{\alpha_0\beta_0}\left|< b/\beta_0 >\right|^2\left|< \alpha_0 / a >\right|^2 \delta\left(\bar{\varepsilon}_F - \varepsilon_{\alpha_0}\right)\delta\left(\varepsilon_{\alpha_0} - \varepsilon_{\beta_0}\right) \\ &= \frac{4\pi e^2}{\hbar}\left|T^0_{AB}\right|^2 \rho_b\left(\bar{\varepsilon}_F\right)\rho_a\left(\bar{\varepsilon}_F\right)\end{aligned} \quad (12)$$

Where $\bar{\varepsilon}_F = \varepsilon_F - eV$

The inelastic conductance in the first order is:

$$\begin{aligned}\frac{\partial I^{(1)}_{inelastic}}{\partial V} &= \\ &= \sum_{\alpha_0\beta_0}\left|T^1_{AB}\right|^2\left|< \alpha_0 / a >\right|^2\left|< b/\beta_0 >\right|^2 \delta\left(\varepsilon_{\beta_0} - \varepsilon_{\alpha_0} - \Omega\right)\cdot\delta\left(\varepsilon_F - eV - \varepsilon_{\alpha_0}\right)\Theta\left(\varepsilon_F - \varepsilon_{\beta_0}\right) \quad (13) \\ &= \left|T^1_{AB}\right|^2 \rho_a\left(\bar{\varepsilon}_F\right)\rho_b\left(\bar{\varepsilon}_F - \Omega\right)\Theta\left(eV - \Omega\right).\end{aligned}$$

The normalized total conductance in the first order is:

$$\left(\frac{\partial I^{(1)}_{elastic}}{\partial V}+\frac{\partial I^{(1)}_{inelastic}}{\partial V}\right)/\frac{\partial I^{(1)}_{elastic}}{\partial V}=1+\eta$$
$$\eta=\frac{\left|T^{1}_{AB}\right|^{2}}{\left|T^{0}_{AB}\right|^{2}}\frac{\rho_b\left(\bar{\varepsilon}_F-\Omega\right)}{\rho_b\left(\bar{\varepsilon}_F\right)}\Theta(eV-\Omega). \qquad (14)$$

We estimate that this formula gives the dominant term in the tunneling current and predict a peak in the second derivative of the tunneling current. Our result is different from the result obtained using the Persson Baratoff formalism, which predicts a dip in the second derivative of the current.

We have evaluated the tunneling currents and conductance [10], corresponding to all individual processes indicated in Fig.2 – 4 .The relevant terms in the total conductance include the interference terms between the first and second order inelastic terms, but also interference between the first and third order elastic terms. In the Persson – Baratoff formalism only the interference terms between the first and third order elastic terms appear. In our model, the interference terms give a complicated formula, but we appreciate that for usual experimental conditions (5 - 10A^{o} separations between the tip and the adsorbate), (14) gives the dominant term.

For low separation the interactions can modify the relative strength in the correction terms in perturbation theory and the correction terms can change the sign of η. An experimental result in which we observe a dip in the inelastic tunneling spectra is obtained by the Fritz Haber Institut group [11].

Also in the previous estimations, the contributions to the tunneling current of the modulation of the barrier by the vibrating molecules are neglected, we consider that in the case of nonresonat electronic tunneling, this effect can be dominant and can explain the experimental results.

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References:

1. Stipe B C, Rezaei M A and Ho W 1998 *Science* **280** 1732
2. Stipe B C, Rezaei M A and Ho W 1999 *Phys. Rev. Lett.* **82** 1724
3. Binnig G, Garcia N and Rohrer H 1985 *Phys. Rev.* B **32** 1336
4. Persson B N J and Demuth J E 1986 *Solid State Comm*. **57** 769
5. Persson B N J and Baratoff A 1987 *Phys. Rev. Lett*. **59** 339
6. Gata M A and Antoniewicz P R 1993 *Phys, Rev.* B **47** 13.797
7. Spataru C and Budau P 1997 *J. of Phys.: Cond. Matter* **9** 8333
8. Mingo N and Makoshi K 2000 *Phys. Rev. Lett*. **84** 3694
9. Lorente N and Persson M 2000 *Phys. Rev. Lett.* 85 2997
10. Budau P (unpublished results)
11. Pasqual J I, Jackiw J J, Song Z, Weiss P S, Conrad H and Rust H P 2001 *Phys. Rev. Lett.* **86** 1050

Figure captions:

Fig.1 *Electrons tunnel from the left (L) electrode (tip) to the right (R) electrode. The corresponding projected densities of states are denoted* $\rho_B(\varepsilon)$ *and* $\rho_A(\varepsilon)$.

Fig.2 *Diagrammatic representations of the matrix elements contributing to the resonant tunneling current in the first order. The circles denotes (as in [5]) the Fermi sea of the tip (*β *states) and the Fermi sea of the adsorbate – substrates system (*α *states).*

Fig.3 *Diagrammatic representations of the matrix elements contributing to the resonant tunneling current in the second order.*

Fig.4 *Elastic third order processes with one or three tunneling electrons. Circled numbers indicate the time ordering of the events.*

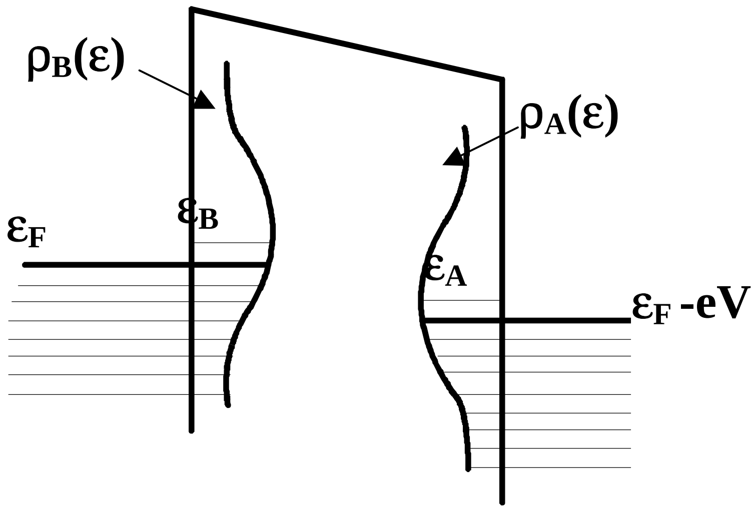

Fig.1

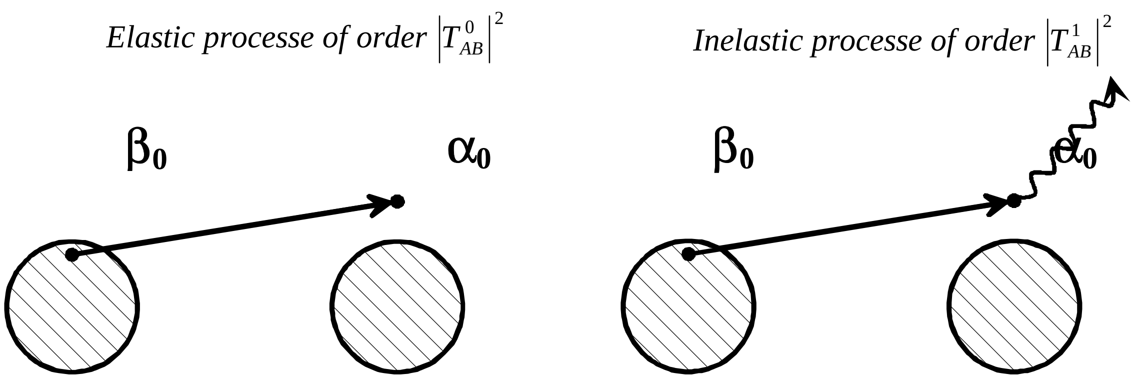
Elastic processe of order $\left|T_{AB}^{0}\right|^{2}$
Inelastic processe of order $\left|T_{AB}^{1}\right|^{2}$
β_0
α_0
β_0
α_0

Fig. 2

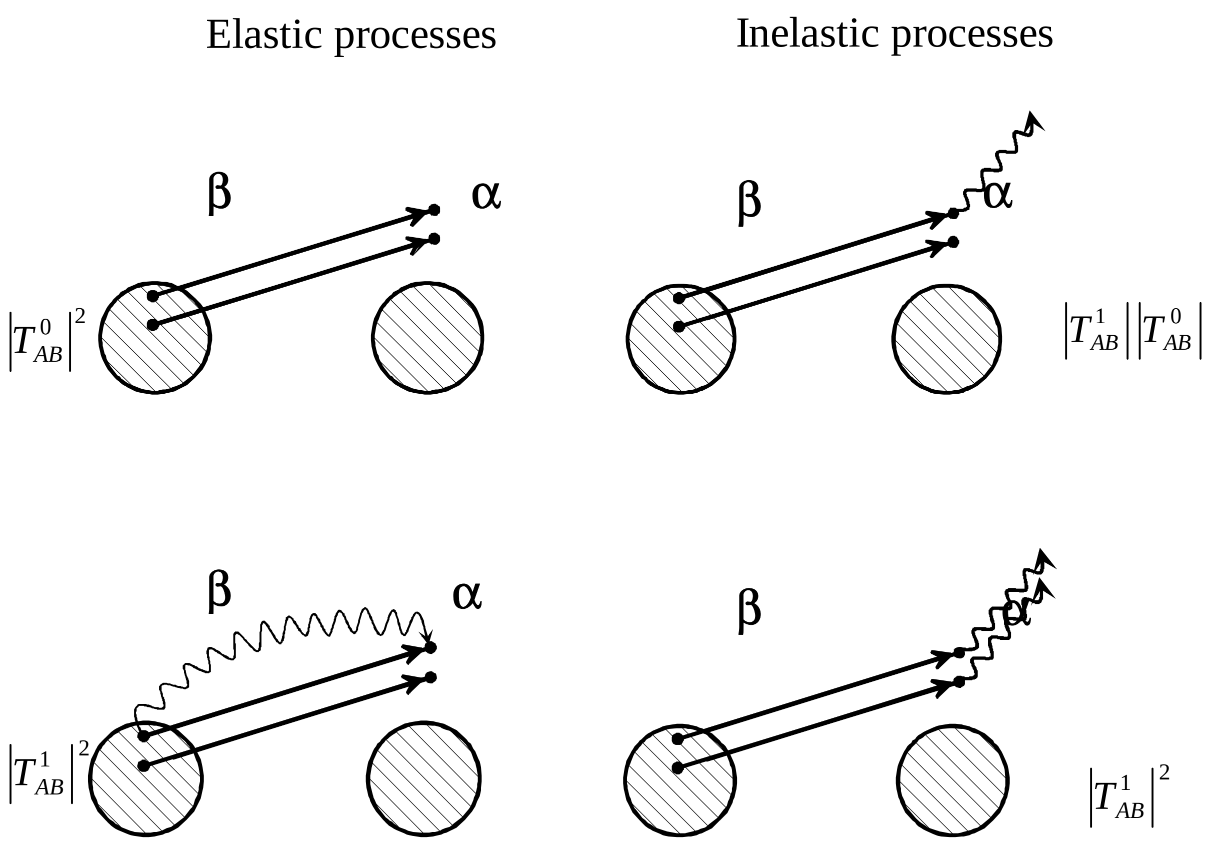
Elastic processes
Inelastic processes
β
α
β
α
$|T_{AB}^0|^2$
$|T_{AB}^1||T_{AB}^0|$
β
α
β
α
$|T_{AB}^1|^2$
$|T_{AB}^1|^2$

Fig. 3

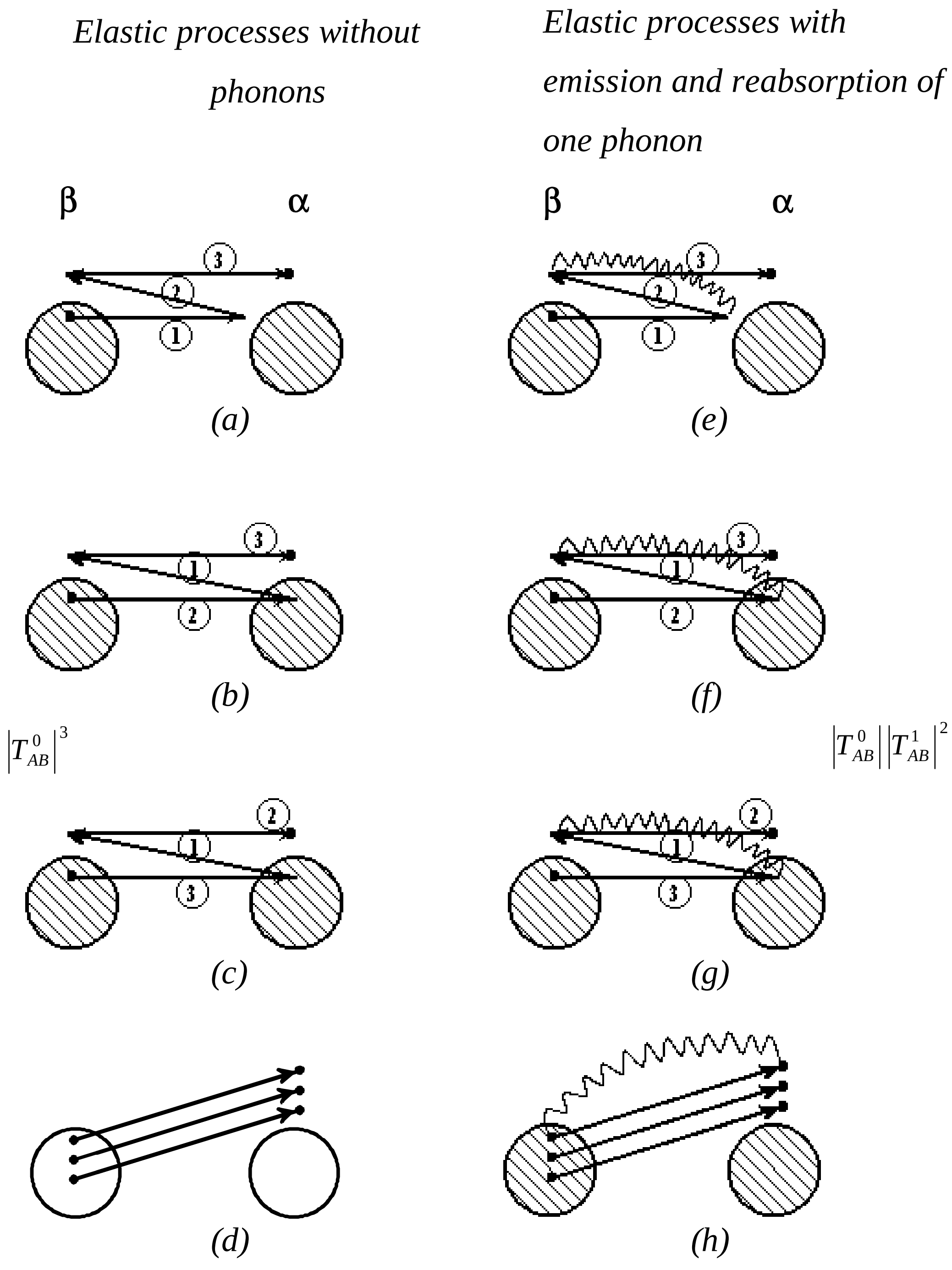
Elastic processes without phonons
Elastic processes with emission and reabsorption of one phonon
β α
β α
(a)
(e)
(b)
(f)
$\left|T_{AB}^{0}\right|^{3}$
$\left|T_{AB}^{0}\right|\left|T_{AB}^{1}\right|^{2}$
(c)
(g)
(d)
(h)

Fig. 4