

# De-excitation of metastable nitrogen molecules on surfaces - quantum kinetic modelling -



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## 1 Motivation

▷ secondary electrons emitted from plasma boundaries are generally very important for the operation of a gas discharge

– dielectric barrier discharges for instance: experimental evidence that stability of the diffusive mode is controlled by seed electrons at the electrodes [1]

▷ up to now not clear how secondary electrons are made available on the microscopic scale

– one possibility: de-excitation of metastables at the boundary with subsequent release of surface electrons (see Fig. 1)

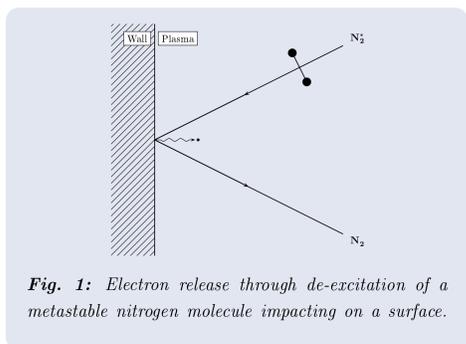


Fig. 1: Electron release through de-excitation of a metastable nitrogen molecule impacting on a surface.

▷ metastable de-excitation process can take place in several possible ways:

- Penning de-excitation
- Penning exchange-process
- direct (resonant) charge transfer
- ...

▷ released electron can emerge from bulk or surface state

▷ total number of released electrons per impacting metastable particle: secondary electron emission coefficient  $\gamma_e$

▷ aim of our investigations: quantum-kinetic simulation of the de-excitation of metastable nitrogen molecules on a dielectric surface (preferably  $Al_2O_3$ ) and calculation of  $\gamma_e$

## 2 Model

▷ we need experimental & theoretical data to compare our results with, so that we can

- validate our approach
- benchmark our calculations and the approximations that may be necessary
- ensure that our description is detailed enough for the plasma context

▷ problem: data available only for  $N_2^*$  de-excitation on Al ([2]) but not on  $Al_2O_3$

▷ therefore we consider Al /  $N_2^*$  system as a starting point

▷ dominant metastable state:  $N_2(^3\Sigma_u^+)$

▷ initial step: investigate Penning de-excitation process (see Fig. 2)

▷ time-dependent non-equilibrium process

▷ hypothesis: process driven by Coulomb interaction between an electron on the molecule and an electron in the solid

▷ approximations:

- ideal planar Al surface extending over the half space  $z < 0$
- metastable molecule:
  - \* two-level system consisting of ground state ('0') & excited state ('1')
  - \* only one single active electron
  - \* motion of the molecule's center  $\vec{R}(t)$  separated from the dynamics of the system and supplied externally (trajectory approximation [3])
- only one single active electron in the solid

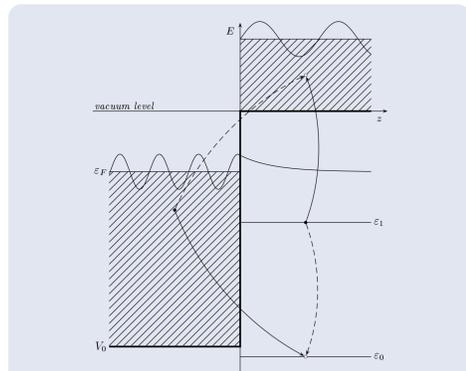


Fig. 2: Schematic of the Penning de-excitation process (solid lines) in an Al /  $N_2$  system showing the electronic structure and the qualitative behaviour of the wave functions. The Penning exchange process is indicated using dashed lines.

▷ model Hamiltonian:

$$H = H_0 + H_1(t) \quad (1)$$

$$H_0 = \sum_{\vec{k}} \varepsilon_{\vec{k}} c_{\vec{k}}^\dagger c_{\vec{k}} + \sum_{\vec{q}} \varepsilon_{\vec{q}} c_{\vec{q}}^\dagger c_{\vec{q}} + \sum_m \varepsilon_0 c_{0m}^\dagger c_{0m} + \sum_m \varepsilon_1 c_{1m}^\dagger c_{1m} \quad (2)$$

$$H_1(t) = \sum_{\vec{k}, \vec{q}, m} \left( V_{0m, \vec{k}}^{\vec{q}, 1m}(t) c_{0m}^\dagger c_{\vec{k}} c_{\vec{q}}^\dagger c_{1m} + h.c. \right) \quad (3)$$

- $\vec{k}$  ... metal electron states
- $\vec{q}$  ... free electron states
- $m$  ... molecular magnetic quantum number

▷ molecule motion contained in  $H_1(t)$

▷ Penning matrix element:

$$V_{0m, \vec{k}}^{\vec{q}, 1m}(t) = \int d\vec{r}' \int d\vec{r}'' \Psi_{0m}^*(\vec{r}' - \vec{R}(t)) \times \Psi_{\vec{k}}(\vec{r}) V_C(|\vec{r} - \vec{r}''|) \Psi_{\vec{q}}^*(\vec{r}'') \Psi_{1m}(\vec{r}' - \vec{R}(t)) \quad (4)$$

▷ to calculate  $V_{0m, \vec{k}}^{\vec{q}, 1m}(t)$  we need wave functions:

- electron on molecule: linear combination of atomic orbitals (LCAO) using hydrogen-like wave functions  $\Rightarrow$  ground state  $2\pi_u$  & excited state  $2\pi_g$

$$\Psi_{0m}(\vec{r}) = \Psi_{2\pi_u^m}(\vec{r}) = \Psi_{2\pi_u^m}^A(\vec{r}) + \Psi_{2\pi_u^m}^B(\vec{r}) \quad (5)$$

$$= \frac{1}{\sqrt{N_{2\pi_u}}} \frac{(-2m)\kappa^{\frac{5}{2}}}{\sqrt{8\pi}} r e^{im\varphi} \times \left( e^{-\kappa\sqrt{r^2+(z+\frac{\rho}{2})^2}} + e^{-\kappa\sqrt{r^2+(z-\frac{\rho}{2})^2}} \right) \quad (6)$$

$$\Psi_{1m}(\vec{r}) = \Psi_{2\pi_g^m}(\vec{r}) = \Psi_{2\pi_g^m}^A(\vec{r}) - \Psi_{2\pi_g^m}^B(\vec{r}) \quad (7)$$

$$= \frac{1}{\sqrt{N_{2\pi_g}}} \frac{(-2m)\kappa^{\frac{5}{2}}}{\sqrt{8\pi}} r e^{im\varphi} \times \left( e^{-\kappa\sqrt{r^2+(z+\frac{\rho}{2})^2}} - e^{-\kappa\sqrt{r^2+(z-\frac{\rho}{2})^2}} \right) \quad (8)$$

- $r, z$  ... cylindrical coordinates,  $\kappa = \frac{3.5}{a_B}$
- $N_{2\pi_{u/g}}$  ... Normalization constants
- $\rho$  ... interatomic distance

– electron in surface: model solid as a potential well with square confining potential step & use box normalization (see also Fig. 2)

$$\Psi_{\vec{k}}(\vec{r}) = \frac{1}{L\sqrt{L}} e^{ik_x x} e^{ik_y y} \Psi_{k_z}(z) \quad (9)$$

$$\Psi_{k_z}(z) = \left( e^{ik_z z} + R_{k_z} e^{-ik_z z} \right) \Theta(-z) + T_{k_z} e^{-\kappa k_z z} \Theta(z) \quad (10)$$

– emitted electron: plane waves (see also Fig. 2)

$$\Psi_{\vec{q}}(\vec{r}) = \frac{1}{L\sqrt{L}} e^{iq\vec{r}} \quad (11)$$

## 3 Quantum kinetics

▷ problem dealt with is an intrinsic non-equilibrium process

▷ we aim to perform a quantum-kinetic simulation of this process

▷ method of choice: Keldysh Green's function technique

▷ generalization of ordinary Green's function technique using a time contour in the complex plane

▷ first step: consider evolution of excited state

▷ equation of motion (Dyson equation) for retarded Green's function (compact notation):

$$G_{1m}^R = G_{1m}^{R(0)} + G_{1m}^{R(0)} \Sigma_{1m}^R G_{1m}^R \quad (12)$$

▷ calculate self energy  $\Sigma_{1m}^R$  in second order perturbation theory (see Fig. 3)  $\Rightarrow$  central function:

$$\Delta_{1m}(t_1, t_2) = \sum_{\vec{k}, \vec{q}} V_{0m, \vec{k}}^{\vec{q}, 1m}(t_1) V_{0m, \vec{k}}^{\vec{q}, 1m}(t_2) n_{\vec{k}}(t_0) \times e^{-i(\varepsilon_0 + \varepsilon_{\vec{q}} - \varepsilon_1 - \varepsilon_{\vec{k}})(t_1 - t_2)} \quad (13)$$

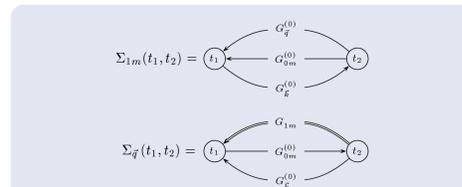


Fig. 3: Second order self energies for an electron in the excited molecule state and the free electron state (note the dressed Green's function  $G_{1m}$ ).

▷ Eq. (12) solvable iteratively

$$G_{1m}^R(t, t') = G_{1m}^{R(0)}(t, t') T_C e^{-\int_{t'}^t dt_1 \int_{t_1}^t dt_2 \Delta_{1m}^R(t_1, t_2)} \quad (14)$$

$\rightsquigarrow$  occupation number of excited state:

$$n_{1m}(t) = \frac{1}{2} - \frac{1}{2} \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \left[ \Delta_{1m}(t_1, t_2) \times T_C e^{-\int_{t_1}^t dt'_1 \int_{t_1}^t dt'_2 \Delta_{1m}^R(t'_1, t'_2)} T_A e^{-\int_{t_2}^t dt'_1 \int_{t_2}^t dt'_2 \Delta_{1m}^A(t'_1, t'_2)} \right] + \frac{1}{2} T_C e^{-\int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \Delta_{1m}^R(t_1, t_2)} T_A e^{-\int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \Delta_{1m}^A(t_1, t_2)} \quad (15)$$

$T_{A/C}$  ... (a)chronological time ordering operator

▷ now consider total number of emitted electrons

$$\gamma_e = \lim_{t \rightarrow \infty} \sum_{\vec{q}} n_{\vec{q}}(t) = \lim_{t \rightarrow \infty} \sum_{\vec{q}} \frac{1}{2} (1 - i F_{\vec{q}}(t, t)) \quad (16)$$

▷ Keldysh component of Green's function  $F_{\vec{q}}(t, t')$ :

$$F_{\vec{q}}(t, t') \approx -i G_{\vec{q}}^{R(0)}(t, t_0) G_{\vec{q}}^{A(0)}(t_0, t') + \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 G_{\vec{q}}^{R(0)}(t, t_1) \Omega_{\vec{q}}(t_1, t_2) G_{\vec{q}}^{A(0)}(t_2, t') \quad (17)$$

▷ Keldysh component of self energy  $\Omega_{\vec{q}}(t, t')$ :

$$\Omega_{\vec{q}}(t, t') = \sum_{\vec{k}, m} V_{0m, \vec{k}}^{\vec{q}, 1m}(t) V_{0m, \vec{k}}^{\vec{q}, 1m}(t')^* \times G_{0m}^{-(0)}(t', t) G_{\vec{k}}^{+-(0)}(t, t') G_{1m}^{+-}(t, t') \quad (18)$$

▷ use full ('dressed') Green's function  $G_{1m}^{+-}$  to incorporate lifetime effects of the excited state

$$G_{1m}^{+-} = \tilde{G}_{1m}^{+-(0)} + G_{1m}^{R(0)} \Sigma_{1m}^{+-} G_{1m}^{+-} \quad (19)$$

▷ can be solved iteratively to give

$$G_{1m}^{+-}(t, t') = G_{1m}^{+-(0)}(t, t') T_C e^{-\int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \Delta_{1m}^R(t_1, t_2)} \times \left[ 1 - \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \Delta_{1m}^A(t_1, t_2) T_A e^{-\int_{t_2}^t dt'_1 \int_{t_2}^t dt'_2 \Delta_{1m}^A(t'_1, t'_2)} \right] \quad (20)$$

▷ total occupation number of free electron states

$$\sum_{\vec{q}} n_{\vec{q}}(t) = \frac{1}{2} \sum_m \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \Delta_{1m}(t_1, t_2) \left[ 1 - \int_{t_0}^t dt'_1 \int_{t_0}^t dt'_2 \Delta_{1m}^A(t'_1, t'_2) T_A e^{-\int_{t'_2}^t dt''_1 \int_{t'_2}^t dt''_2 \Delta_{1m}^A(t''_1, t''_2)} \right] \times T_C e^{-\int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \Delta_{1m}^R(t_1, t_2)} \quad (21)$$

▷ for a time-local self energy  $\Delta_{1m}(t_1, t_2) \sim \delta(t_1 - t_2)$  this reduces to results published by Makoshi [4]

▷ Eq. (21) too complex to be calculated numerically in considerable time  $\Rightarrow$  physically motivated approximations necessary

## 4 Matrix element

▷ can be calculated numerically from Eq. (4)

▷ to make final result (Eq. (21)) tractable numerically, it would be desirable to separate  $\vec{k}$  &  $\vec{q}$  dependent terms from the matrix element calculation

▷ only possible through approximations

– long-wavelength approximation:

- \* assume  $\varepsilon_{\vec{q}}$  small  $\Rightarrow \lambda_{\vec{q}}$  big
- \*  $\Psi_{\vec{q}}$  can be taken at the molecule's center  $\vec{R}(t)$  and moved in front of the integral

– metal wave function decreases exponentially outside the solid on a scale large compared to the molecule's bond length (see Eq. (10) and Fig. 2)  $\Rightarrow$  expand  $\Psi_{\vec{k}}$  around molecule's center

▷ in addition: variable transform:  $\vec{r} \rightarrow \vec{r} + \vec{R} \Rightarrow$  time-dependence shifted to  $\vec{k}$  &  $\vec{q}$  dependent terms

▷ final structure:

$$V_{0m, \vec{k}}^{\vec{q}, 1m}(t) = V_{\vec{k}}(t) V_{\vec{q}}(t) V_m \quad (22)$$

$$V_{\vec{k}}(t) = -\kappa_{k_z} \Psi_{\vec{k}}(\vec{R}(t)) \quad (23)$$

$$V_{\vec{q}}(t) = \Psi_{\vec{q}}^*(\vec{R}(t)) \quad (24)$$

$$V_m = \int d\vec{r}' \int d\vec{r}'' z \Psi_{0m}^*(\vec{r}) V_C(|\vec{r} - \vec{r}''|) \Psi_{1m}(\vec{r}'') \quad (25)$$

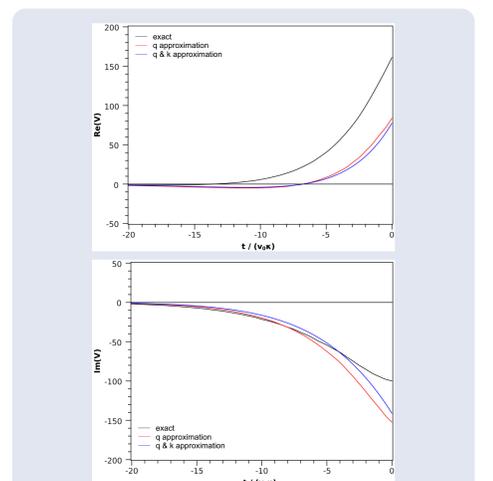


Fig. 4: Real and imaginary part of the matrix element in arbitrary units (exact and with approximations) for a normal incidence molecule trajectory at  $\vec{k} = \frac{1}{5}(k_{max} - k_{min})\vec{e}_z$ ,  $\vec{q} = |\vec{q}|\vec{e}_z$  (explicit energy conservation assumed),  $m = 1$ . Apparently the applied approximations are good for larger times and distances from the surface ( $t \geq \frac{10}{v_{Fq}}$  /  $z \geq 4a_B$ ).

## 5 Outlook

▷ finish calculation with approximated matrix element & compare results with [2]

▷ repeat calculation for dielectric surface

▷ dielectric has different energy scheme compared to Fig. 2  $\Rightarrow$  different processes possible (e.g. direct charge transfer  $\Rightarrow$  temporary negative ions)

▷ we need to adjust our approximations for a dielectric surface

## 6 References

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