Vibrationally inelastic collisions of slow electrons with polyatomic molecules

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Abstract. We present a computational method developed for calculations of vibrationally inelastic collisions of electrons with polyatomic molecules. The method is first applied to calculate vibrational excitations of cyclopropane molecule. In second step we demonstrate how the method can be altered for collisions at higher energies, namely 50—300 eV. In the case of furan molecule we compare a size of summed vibrationally inelastic cross sections with the elastic data. For the two molecules studied we also compare our calculated results with the available experimental data.

1. Introduction
During the last two decades the modeling of elastic collisions of electrons with polyatomic molecules became a well-established task. Many authors report fixed-nuclear elastic data obtained by use of R-matrix method [1, 2], complex Kohn variational method [3, 4], Schwinger multichannel method [5, 6, 7], or optical potential method with single-center expansion of electron wave function [8, 9].

However, the situation is quite different in computational modeling of the inelastic processes during the collision. In case of vibrational excitation there have been many rigorous and successful attempts for diatomic [10, 11, 12, 13] and triatomic [14, 15, 16] molecules but very few results are available for the polyatomic systems. We believe that at present state a treatment of electron-impact vibrational excitation of polyatomic molecules requires several numerically controlled approximations. In the presented method (Discrete Momentum Representation) we show that it is still possible to retain both the rigor of the theory and computational feasibility.

Some of the lighter hydrocarbons are known as sources of carbon atoms during chemical vapor decomposition reactions. The cyclopropane was detected in cooler edges of the fusion plasmas. The most marked feature observed by experiments [17] has to do with the excitation of ν3 vibration, the C-C ring stretching. The molecule was previously studied computationally [18], however due to the model limitations only three full-symmetric vibrational modes were studied. Therefore, we employed Discrete Momentum Representation (DMR) method [16] to calculate cross sections for excitation of all the vibrational modes.

The motivation to study electron interactions with furan molecules (C₄H₄O) in recent years predominantly comes from radiation damage research, since its structure may be considered as a simple representative of the sugar component in the DNA backbone. Hence, the aim of the present study is to simplify the DMR method for higher collision energies (by use of unitarized
Born approximation) and attempt to estimate a probability of deposition of electron collision energy into vibrational motion of the target furan molecule. The collision energy range of our interest is 50–300 eV.

2. Theory

2.1. Overview of the DMR Method

The vibrationally inelastic DMR method was discussed in detail in Ref. [16] and only a brief summary is given here. We made use of the following approximations:

- We introduce one-electron optical potential $\hat{V}$ for the interaction between the scattered electron and the charge density of the molecule. Moreover, we retain only the first term of the optical potential expansion (see for example Ref. [19]), ending up with the static-exchange (SE) approximation.

- The SE approximation is corrected by a model DFT potential $V_{cp}$ that accounts for orbital relaxation of the bound electrons and for the correlation between the scattered electron and the bound electrons. We used the interpolation formula suggested by Perdew and Zunger [20].

- Nuclear dynamics is described by the rotationally frozen and vibrationally harmonic approximations. Moreover, for the vibrational space of each normal mode we use only a two-state approximation.

These approximations allow us to describe the scattering problem via the two-channel Lippmann-Schwinger equation in the three-dimensional momentum space:

$$\langle \chi_1 k_1 | \hat{T} | \chi_0 k_0 \rangle = \langle \chi_1 k_1 | \hat{U} | \chi_0 k_0 \rangle + \sum_{i=0}^{1} \int dk \frac{\langle \chi_1 k_1 | \hat{U} | \chi_i k \rangle \langle \chi_i k | \hat{T} | \chi_0 k_0 \rangle}{k_0^2 - 2E_i - k^2 + i\epsilon},$$

(1)

where $\hat{U}$ stands for twice the interaction potential $\hat{V}$, $E_0 = 0$ (for the elastic channel) is the energy of the vibrational ground state and $E_1$ is the energy of the first excited vibrational state. These two states are described by the vibrational functions $\chi_0$ and $\chi_1$, respectively. The vectors $k_0$ and $k_1$ represent the plane-wave functions for the incoming and outgoing electrons, respectively.

Numerical discretization ($p$ and $i$ run through abscessas of the radial and angular quadratures, respectively)

$$\int dk \int d\hat{k} g(k) \rightarrow \sum_p w_p \sum_i w_i g(k_{pi})$$

(2)

of the integral on the r.h.s of the Eq. (1) leads to a set of two coupled matrix equations:

$$\begin{pmatrix} T_{00} & T_{01} \\ T_{01} & T_{11} \end{pmatrix} = \begin{pmatrix} U_{00} & U_{01} \\ U_{10} & U_{11} \end{pmatrix} + \begin{pmatrix} U_{00} & U_{01} \\ U_{10} & U_{11} \end{pmatrix} \cdot \begin{pmatrix} G_0 & 0 \\ 0 & G_1 \end{pmatrix} \cdot \begin{pmatrix} T_{00} & T_{01} \\ T_{10} & T_{11} \end{pmatrix},$$

(3)

with the interaction matrix elements defined as follows:

$$[U_{00}]_{pi,qj} = \langle \chi_0 k_{pi} | \hat{U} | \chi_0 k_{qj} \rangle$$

$$[U_{11}]_{pi,qj} = \langle \chi_1 k_{pi} | \hat{U} | \chi_1 k_{qj} \rangle$$

$$[U_{01}]_{pi,qj} = \langle \chi_0 k_{pi} | \hat{U} | \chi_1 k_{qj} \rangle = [U_{10}]_{pi,qj}.$$  

The body-fixed scattering amplitudes for the vibrational transitions are obtained by the matrix inversion in equation (3). More details about the evaluation of the matrix elements (4) and the quadrature scheme (2) of the singular kernels on r.h.s of the Eq. (1) can be found in Refs. [16, 21].
2.2. Unitarized First Born Approximation

In a case of weak interactions or higher collision energies the Eq. (1) may be simplified by neglecting the second term on the r.h.s. Such an approximation is called first Born approximation (FBA). It is clear that in the FBA elastic and inelastic channels are considered independent as their scattering amplitudes are given by simple potential matrix elements

\[ f_{\text{FBA}}^{\text{ela}}(\nu_0 k_1 \leftarrow \nu_0 k_0) = -4\pi^2 \langle \nu_0 k_1 | \hat{V} | \nu_0 k_0 \rangle , \]
\[ f_{\text{FBA}}^{\text{inela}}(\nu_1 k_1 \leftarrow \nu_0 k_0) = -4\pi^2 \langle \nu_1 k_1 | \hat{V} | \nu_0 k_0 \rangle . \]

One of drawbacks of the FBA model is that it breaks the unitarity of the scattering matrix which is connected to a flux conservation during the scattering process. Therefore we implemented unitarized first Born approximation (UFBA). The UFBA represents the FBA of a K-matrix (instead of T-matrix approximated above). In this way the approximated hermitian K-matrix leads to a unitary S-matrix and therefore conservation of the scattering flux.

The usefulness of this approach was first demonstrated by Itikawa [22], and it has been later noted that the UFBA often yields results for scattering cross sections that are significantly more accurate than those obtained by the FBA [23]. The two-channel FBA K-matrix can be written as (we use the plane-wave normalization instead of the more common energy normalization)

\[ \langle \nu_i k_1 | K | \nu_j k_0 \rangle \approx -\pi \langle \nu_i k_1 | \hat{V} | \nu_j k_0 \rangle , \quad i, j = 0, 1. \]

The unitarized first Born T-matrix \( T^U \) is then obtained by means of Heitler’s integral equation [24]:

\[ \pi T^U = -K (1 - iK)^{-1} . \]

The elastic and inelastic scattering amplitudes are directly proportional to the parts of \( T^U \) as

\[ f_{\text{ela}}^U(\nu_0 k_1 \leftarrow \nu_0 k_0) = -4\pi^2 \langle \nu_0 k_1 | T^U | \nu_0 k_0 \rangle , \]
\[ f_{\text{inela}}^U(\nu_1 k_1 \leftarrow \nu_0 k_0) = -4\pi^2 \langle \nu_1 k_1 | T^U | \nu_0 k_0 \rangle . \]

It should be pointed out that the UFBA is an approximation using full static-exchange potential and it should not be confused with the (first) dipole Born approximation used in the literature, as the latter employs only a dipole potential that predicts zero cross sections for infrared inactive modes.

3. Results

3.1. Cyclopropane

Electronic state of the target molecule was described at Hartree-Fock level. We used Gaussian type orbital basis set of DZP quality. Polarizability tensor components used in the present calculations were obtained as linear response functions in Kohn-Sham DFT [29] calculations with B3LYP hybrid functional and Sadlej’s polarized VTZ basis sets [30] as implemented in program Dalton Release 2.0 (2005). Body frame of reference was chosen by principal axes, thus the calculated polarizability tensor is diagonal:

\[ \alpha(\text{C}_3\text{H}_6) = \begin{pmatrix} 38.8 \\ 38.8 \\ 33.8 \end{pmatrix} . \]

The tensor compares favorably with the experimentally measured value of spherical polarizability \( \alpha_0 = 38.2 \) a.u. [31].

Figure 1 displays a computed integral cross sections with the present DMR method at static-exchange (DMR SE) and static-exchange + polarization (DMR SEP) levels. It can be seen
Figure 1. Elastic integral cross section of cyclopropane. The experimental data of Nishimura et al 1991 [25] are denoted by crosses, circles are taken from Szmytkowski et al 2002 [26] and the rectangles are from Makochekanwa et al 2006 [27]. Previous computations of Curik and Gianturco 2002 [28] are shown as dot-dashed curve. Present results in static-exchange approximation are displayed by dashed curve while the calculations with static-exchange + polarization model are shown as full curve.

Figure 2. The measured spectrum shown as crosses was taken from Ref. [17]. Computed EELS spectrum (with half-width of 16 meV) is displayed as full line. Experimental data [17] were normalized at the elastic peak.
that correlation-polarization forces strongly affect even the elastic scattering process at collision energies under 15 eV. Our results are compared with previous experimental and theoretical data.

The cyclopropane molecule has 21 vibrational modes. Out of them only 14 are unique due to high symmetry of the molecule. We calculated vibrational excitation cross sections of all the modes. In order to compare the data with an experiment we have decided to reconstruct an experimentally measured electron energy-loss spectrum (EELS). The energy resolution half-width was set to 16 meV. As a shape for the resolution function we choose the Gaussian function. A comparison of such computed EELS and the experimental measurement is shown in Fig. 2. Because the experimental EELS data in [17] were not in absolute values we normalized them to our computed elastic peak. We conclude that the agreement is exceptionally good.

3.2. Furan

Electronic target state is once again described by Hartree-Fock theory. The Slater-type wave function then generates electrostatic and exchange interaction with continuum electron. Since the collision energies of our interest here start at 50 eV and reach 300 eV we can neglect the correlation-polarization interaction with impunity. Furan belongs to $C_{2v}$ symmetry, therefore it has 21 non-degenerate vibrational modes and most of them are infrared active.

![Figure 3](image)

Figure 3. Rotationally summed $0 \rightarrow 1$ vibrationally inelastic absolute differential cross section for scattering of the electrons by furan. All 21 excitation modes are plotted. Sum of all the vibrational excitation cross sections is displayed as a thick curve.

It has been discussed previously [32] that vibrational excitations should not affect significantly elastic differential cross section (DCS) in the present high energy range. Still, according to our knowledge, an explicit estimation of the absolute DCSs for vibrational excitation of similar molecules (representing building blocks of large biopolymers) and for the present incident energy range has not been reported. The calculated UFBA rotationally summed $0 \rightarrow 1$ vibrationally inelastic differential cross sections are shown in Fig. 3. The selected set of collision energies is 50, 100, 150, 200, 250 and 300 eV. The cross sections were calculated according to formula (10).

The resulting data were used in Ref. [33] to estimate the ratio between a probability of the deposition of collision energy into vibrational motion of furan during the collision process and
a probability that the electron undergoes elastic scattering. Authors concluded that the above mentioned ratio as a function of the scattering angle may reach about 10% in the examined collision energy range of 50–300 eV.

4. Summary
In present work we applied the DMR method for two different inelastic studies. We summarized the approximations used in the method and then we have shown that their use still leads to results of a very good quality.

In first we calculated electron impact vibrational excitation of cyclopropane. All the vibrational modes were computed. The elastic and inelastic data agree very well with the available experimental data. In second we attempted to estimate the size of cross section for deposition of collision energy into vibrational modes of furan. The basic DMR method for this problem was simplified by UFBA that can be well justified by a weak nature of the inelastic interaction together with higher collision energies (50–300 eV). We conclude that in this energy range the size of total vibrationally inelastic cross section reaches about 10% of the elastic probability.

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