Probing Electron Correlation and Nuclear Dynamics in Momentum Space

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Abstract. Orbital imaging experiments employing Electron Momentum Spectroscopy are subject to many complications, such as distorted wave effects, conformational mobility in the electronic ground state, ultra-fast nuclear dynamics in the final state, or a dispersion of the ionization intensity over electronically excited (shake-up) configurations of the cation. The purpose of the present contribution is to illustrate how a proper treatment of these complications enables us to probe in momentum space the consequences of electron correlation and nuclear dynamics in neutral and cationic states.

1. Introduction
An everlasting dilemma in quantum mechanics pertains to the physical relevance of orbitals, or orbital densities. Assuming that the Born (sudden), binary encounter, and plane wave impulse approximations are valid, spherically averaged Dyson orbital densities relating to transition amplitudes between neutral and ionized states (eq. 1) can be experimentally reconstructed in momentum space by means of Electron Momentum Spectroscopy (EMS) [1], from the angular dependence (eq. 2) of cross sections in (e, 2e) electron-impact ionization experiments at high kinetic energies (Figure 1). In most applications, (normalized) Dyson orbitals are replaced by standard Kohn-Sham orbitals. However, as with any ionization experiment, analyses of EMS measurements are subject to many complications, such as distorted wave effects, conformational mobility in the neutral ground state along with the usually strong influence of the molecular conformation on electron binding energies, electron correlation and relaxation, dispersion of the ionization intensity over electronic (shake-up) excited states of the cation, and ultra-fast nuclear dynamics in the final ionized state. The main conclusions of two “school case” studies are summarized in the present contribution, in order to illustrate the assertion that, if it has to have any value at all, the interpretation of EMS experiments requires extensive theoretical work.

\[ \sigma_n(p) \propto \left| \int d\Omega g_n(p) \right|^2 = \int d\Omega \left| e^{i\mathbf{p} \cdot \mathbf{r}} \mathbf{\rho}^{N-1} \right|^2 \]

\[ p = \sqrt{(2p_1 \cos \theta - p_0)^2 + (2p_1 \sin \theta \sin(\phi/2))^2} \]

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We first consider a most puzzling discrepancy [2, 3] between the results of a model assuming thermal equilibrium between the gauche and trans conformers (relating to $C_1$ and $C_s$ energy minima) and the experimentally inferred momentum distribution (MD) for the highest occupied molecular orbital (HOMO) of ethanol (Figure 2). This discrepancy cannot be due [4] to (1) a breakdown of the Plane Wave Impulse Approximation (the experimentally inferred MD does not depend much upon $E_0$, the kinetic energy of the impinging electron); (2) a defect in the treatment of electronic correlation and relaxation (comparison with benchmark ADC(3) Dyson orbitals shows that the target Kohn-Sham approximation is valid); (3) a breakdown of the one-electron picture of ionization (the corresponding ADC(3) pole strength exceeds 0.90); (4) some energy overlap with higher lying bands (the energy interval with the next band exceeds 1.6 eV); (5) tunneling effects across a shallow but wide hydroxyl torsion barrier of ~1.15 kcal/mol (the rate of which is estimated to be of one transition per 333 ps, compared with a thermal conversion rate around 5.6 ps$^{-1}$ at 298K); (6) a dimerization of the molecule under high vacuum conditions (a process which should affect all momentum distributions, at odds with the experimental evidence). In view of the flatness of the conformational energy map characterizing ethanol, one of the most tempting explanations resides in thermally induced molecular motions and conformational disorder in the ground state [2, 3]. As shall be shown, molecular relaxation processes induced by ionization have also to be accounted for [4], in order to reconcile theory with experiment.

Our second scope is to refute conclusions drawn by Saha, Wang, et al in [5] regarding fingerprints of the gauche ($C_2$) conformational isomer of 1,3-butadiene ($CH_2=CH-CH=CH_2$) in electron momentum distributions that were experimentally inferred from gas phase (e, 2e) measurements on this compound [6]. Because of enthalpy and entropy difference of 2.93 kcal mol$^{-1}$ and 3.98 cal mol$^{-1}$ K$^{-1}$ in favour of...
the trans-conformer, of C$_{2h}$ symmetry, this conclusion implies that, if we assume that EMS experiments remain subject to the laws of statistical thermodynamics, and that, prior to ionization, the molecule resides in its electronic ground state, some of the EMS experiments which have been analyzed by Saha, Wang et al should have been conducted at temperatures far above 1000K. This most astonishing conclusion was the result [7] of an erroneous assignment of spectral bands due to the neglect of shake-up satellites as well as of the strong influence of the molecular conformation on the ionization spectrum.

2. Ethanol
2.1. Methodology
Spherically averaged momentum distributions (SAMD’s) have been computed for the Highest Occupied Molecular Orbital (HOMO) of ethanol, according to the target Kohn-Sham (B3LYP/aug-cc-pVTZ) approximation. Resolution folding was accounted for, according to the characteristics of the employed (e, 2e) spectrometer ($\Delta p \sim 0.16$ a.u. FWHM) at Tsinghua University, Beijing [2]. Three models [3, 4] have been considered for evaluating the outcome of nuclear dynamics in the ground state, on the basis of a thermal averaging of internal molecular motions and of their influence on the SAMD’s: (1) statistical thermodynamics (beyond the RRHO level), assuming thermal equilibrium between the C$_1$ and C$_s$ conformers; (2) thermal averaging over a “one-dimensional” (1D) subset of 72 nuclear configurations characterized by $\alpha = -180^\circ, -175^\circ, \ldots, +170^\circ, +175^\circ$, and (3) thermal averaging over a “two-dimensional” (2D) subset of 1728 nuclear configurations characterized by $\alpha = -180^\circ, -175^\circ, \ldots, +170^\circ, +175^\circ$, along with $\theta = -60^\circ, -55^\circ, \ldots, +50^\circ, +55^\circ$. Assuming that these configurations are independent enables us to correspondingly calculate their weight at $T=298$K according to:

$$w_i(\alpha) = \frac{e^{-E(\alpha)/k_BT}}{\sum_{i=1}^{72} e^{-E(\alpha)/k_BT}}$$  \hspace{1cm} (3)$$

or $$w_i(\alpha,\theta) = \frac{e^{-E(\alpha,\theta)/k_BT}}{\sum_{i=1}^{1728} e^{-E(\alpha,\theta)/k_BT}}$$  \hspace{1cm} (4)$$

The influence of nuclear dynamics (i.e. structural relaxation effects) in the final ionized state has been modelled using the HOMO of the neutral upon the B3LYP/aug-cc-pVTZ geometry of the radical cation. Furthermore, the evolution of the system immediately after ionization has been studied according to Born-Oppenheimer Molecular Dynamics (BOMD) simulations, at the B3LYP/aug-cc-pVQZ level, using trajectory and integration step sizes of 0.250 a.u. and 0.2 fs, the Bulirsch-Stoer integration scheme along with an integration correction scheme using fifth-order polynomial fit, and assuming a temperature of 0K, that is, the only source of kinetic energy immediately after ionization is assumed to exclusively arise from potential energy gradients. Changes in chemical connectedness have been correspondingly studied using Natural Bond Orbitals.

3.2. Results and Discussion
The flatness of the conformational energy map of ethanol is found to result into significant broadening of conformer populations (Figure 3a). We note that the HOMO of ethanol pertains to a localized oxygen lone pair. Therefore (Figure 3b), significant changes in the outermost momentum distributions reflecting the development of anomeric interactions occur upon rotations of the hydroxyl group ($\alpha$ torsion angle), whereas only marginal changes are induced by methyl rotations ($\theta$). Thermal fluctuations in the electronic ground state alone do not improve agreement between theory and experiment (Figure 4), but are found to significantly populate the nuclear configurations around $\alpha = \pm 90^\circ$. It is worth noticing therefore that structural relaxation in the adiabatic cationic state increases by a factor 4 (!) the outermost electron momentum density at $p \to 0$, due to a rotation of the OH bond to $\alpha = 90^\circ$, along with an increase of the C-C bond length from $\sim 1.50$ to 1.76 Å, and an enhancement thereby of anomeric [$n_0 - \sigma_{O-C,C}$] interactions (Figure 4). Lacking any other satisfactory explanation,
one has to wonder therefore whether the experimental turn-up of (e, 2e) intensities at $p \to 0$ reflects nuclear dynamics induced by the ionization process (i.e. nuclear dynamics in the final state), and whether these structural changes occur fast enough to be detectable in electron impact ionization experiments at high kinetic energies [$E_0=1.2$ keV].

Upon analyzing the results of BOMD calculations for the radical cation (Figure 5), it appears that significant nuclear dynamics is impeded by $C_s$ symmetry when $\alpha=0^\circ$ (trans conformation), whereas hydroxyl rotations are a prerequisite for ultra-fast nuclear dynamics in the final ionized state, in the form of a stretching of the C-C bond by ~0.25 Å and ~0.60 Å upon time intervals of 13 fs and 40 fs, respectively, when $\alpha(t=0)$ is around ±90°. Therefore, incomplete relaxation processes ought to be sufficient for unravelling the discrepancy between the theoretical and experimental momentum distributions characterizing the outermost orbital of ethanol. In particular, according to the computed BOMD trajectories and detailed B3LYP/aug-cc-pVTZ calculations of the outermost momentum distributions of the ethanol radical cation under the constraints of fixed torsion angles ($\alpha=90^\circ$ and $\theta=0^\circ$), the missing fraction (40%) of relative ionization intensity at $p \to 0$ could be recovered upon an inferred time scale of the order of ~8 fs only for the (e, 2e) ionization process, considering the dependence (eq. 5) of the momentum density for the HOMO at $p \to 0$ as a function of the length of the C-C bond ($x$):

$$\sigma_{\text{HOMO}}(p \to 0) = 4.9143x^4 - 33.013x^3 + 82.279x^2 - 89.93x + 36.399 \quad (R^2 = 0.994)$$

\[\text{Figure 3.} \text{ Conformer distributions (a) and influence of hydroxyl (\(\alpha\)) rotations upon the outermost electron momentum distribution (b) of ethanol.}\]

\[\text{Figure 4.} \text{ Theoretical versus experimental (e, 2e) outermost momentum distributions of ethanol (left) and structural changes induced by an adiabatic ionization process (right).}\]
Immediately after ionization, strong oscillations by ~120° of the hydroxyl torsion angle are also noted when ~60° < α(t=0) < ~120°, along with rapid oscillations in the length of the C-O bond, by 0.12 Å, with periods around 40 fs. These observations are consistent with a breaking of the C-C bond and with the formation of a double bond between the C and O atoms.

Figure 5. Evolution of the length of the C-C bond immediately after ionization, according to an analysis of BOMD trajectories for various initial configurations.

Table 1. Evolution of atomic charges and Wiberg bond indices as a function of the length of the C-C bond in CH$_3$-CH$_2$OH$^+$

| C-C bond length (Å) | Atomic charge | Electric charge | Wiberg indices |
|---------------------|---------------|-----------------|----------------|
|                     | $C_1$ | $C_2$ | $O_3$ | $H_4$ | $CH_3$ | $CH_2OH^+$ | $C_1$-$C_2$ | $C_2$-$O_3$ | $O_3$-$H_4$ |
| 1.52$^a$           | -0.676 | -0.080 | -0.768 | 0.473 | - | 1.033 | 0.929 | 0.760 |
| 1.51$^b$           | -0.666 | -0.079 | -0.776 | 0.479 | - | 1.037 | 0.922 | 0.759 |
| 1.76               | -0.470 | -0.010 | -0.428 | 0.543 | 0.340 | 0.660 | 0.617 | 1.148 | 0.686 |
| 2.26               | -0.364 | 0.160 | -0.542 | 0.544 | 0.344 | 0.656 | 0.306 | 1.312 | 0.682 |
| 2.76               | -0.377 | 0.252 | -0.542 | 0.550 | 0.267 | 0.733 | 0.187 | 1.396 | 0.675 |
| 3.26               | -0.390 | 0.296 | -0.535 | 0.553 | 0.223 | 0.777 | 0.145 | 1.430 | 0.671 |
| 3.76               | -0.388 | 0.313 | -0.533 | 0.554 | 0.207 | 0.793 | 0.131 | 1.444 | 0.669 |
| 4.26               | -0.377 | 0.317 | -0.534 | 0.555 | 0.207 | 0.793 | 0.129 | 1.444 | 0.669 |
| 4.76               | -0.363 | 0.315 | -0.536 | 0.554 | 0.216 | 0.784 | 0.132 | 1.437 | 0.670 |
| 5.26               | -0.350 | 0.310 | -0.538 | 0.553 | 0.226 | 0.774 | 0.135 | 1.430 | 0.671 |
| ∞$^c$              | -0.533 | 0.438 | -0.495 | 0.571 | 0 | 1 | - | - | - |

$^a$ Gauche conformer (B3LYP/aug-cc-pVTZ geometry); initial neutral ground state.  
$^b$ Trans conformer (B3LYP/aug-cc-pVTZ geometry); initial neutral ground state.  
$^c$ Results from separate B3LYP/aug-cc-pVDZ calculations upon CH$_3$ and CH$_2$OH$^+$

B3LYP/aug-cc-pVDZ Natural Bond Orbital calculations of Wiberg bond indices and atomic charges (Table 1) correspondingly indicate that the above reorganization of the molecular structure immediately after ionization corresponds to the very first stage of a dissociation of the ethanol radical cation ([CH$_3$-CH$_2$-OH]$^+$) into a methyl radical (CH$_3$) and a protonated form of formaldehyde (H$_2$C=O-H$^+$). Indeed, due to the lack of resolution in energy in EMS experiments, as well as natural
and vibrational broadenings, there will always be huge excesses of energy available, in the form of vibrations, which can easily convert into dissociation over an energy barrier of ~18.2 kcal/mol only. A residual Wiberg bond order of ~0.1 remains at $R_{[C-C]}=5.26 \text{ Å}$ (Table 1), reflecting a charge transfer interaction between the HOMO (C$_2p$ orbital) of the methyl radical and the LUMO ($\pi^*$ orbital) of H$_2$C=O-H$^+$ (Figure 6). The displacement of the outermost electron densities towards the C-C bond and methyl group, which the rise of experimental (e, 2e) ionization intensities at $p \rightarrow 0$ most presumably reflects as a result of the enhancement of $n_O - \sigma_{C-C}$ anomic interactions, therefore images a charge (electron) transfer, from the oxygen lone pair to the methyl group, during an ultra-fast stretching, and possibly cleavage, of the C-C bond.

Figure 6. Evolution of the HOMO of CH$_3$-CH$_2$-OH$^+$ upon a stretching of the C-C bond

3. 1,3-butadiene

3.1. Methodology.
Spherically averaged Dyson orbitals momentum distributions have been computed for all resolvable ionization bands, using Feynman-Dyson transition amplitudes obtained as by-products of one-particle Green’s Function calculations of the valence ionization spectrum of trans-1,3-butadiene, using the benchmark third-order Algebraic Diagrammatic Construction scheme [ADC(3)], in conjunction with Roos’s augmented double-$\zeta$ basis set of atomic natural orbitals, on the basis of B3LYP/TZVP geometrical parameters. The molar fraction of the gauche form of 1,3-butadiene is known to be around 5% at 298K, and can be neglected therefore.

3.2 Results and Discussion.
The ADC(3) valence ionization spectrum of the gauche conformer is totally incompatible [7] with high-resolution photoelectron measurements employing a synchrotron radiation beam [8]. On the other hand, the ADC(3) calculations provide quantitative insights, within ~0.3 eV accuracy, into the available experimental ionization energies and related electron momentum distributions, and this throughout the (outer- and inner-) valence region. In particular, we note (Figure 7) a dramatic improvement in the quality of the description of the (e, 2e) momentum profile inferred from an ionization band at 13.9 eV, when taking into account the contribution of an intense shake-up satellite (S1), with a spectroscopic strength of 0.29, which corresponds to the 1b$_g^{-1}$ 2a$_u^{-1}$ excited configuration of the cation. The conclusion by Saha, Wang et al that several experimentally inferred (e, 2e) momentum distributions “are, in fact, engaged with” the gauche conformer of 1,3-butadiene [5] was the result of many redhibitory mistakes in their assignment of ionization bands (see Figure 8 and ref. 7 for details), due to the neglect of the influence of the conformation on the energy order of ionization lines. We note in particular that the outermost and second ionization bands at 9.2 and 11.5 eV were related to the 7b and 8a ionization lines of the gauche conformer, at 11.2 and 9.1 eV, respectively! Further similar mismatches were noted [7] for two bands (4 and 5) at higher electron binding energies. Also, the presence of the low-lying 1b$_g^{-1}$ 2a$_u^{-1}$ shake-up line at ~13.1 eV was neglected. At last, Saha, Wang et al did not consider that the gaussian bands 2 and 3 in the deconvoluted spectrum (Figures 8a and b) too strongly overlap to permit a reliable enough separate analysis of the underlying intensities.
Figure 7. ADC(3)/aug-ANO Dyson orbital analysis of the momentum density distribution characterizing the band at 13.9 eV in the EMS ionization spectrum [6] of 1,3-butadiene.

Figure 8. Comparison of the EMS ionization spectra at $\phi=0^\circ$ (a) and $\phi=10^\circ$ (b) with ADC(3)/aug-ANO simulations for the trans (c) and gauche (d) forms of 1,3-butadiene. Colors refer to the assignment proposed by Saha, Wang et al in ref. 5.
Conclusion and outlook for the future
A review of EMS measurements on 1,3-butadiene and ethanol demonstrates that thorough theoretical studies are mandatory for reliably interpreting “orbital imaging” experiments that may be subject to many complications, such as electron correlation and relaxation, and a dispersion thereby of the ionization intensity over electronically excited (shake-up) configurations of the cation, distorted wave effects, conformational mobility in the electronic ground state, and the influence thereby of the conformation on ionization energies, as well as nuclear dynamics in the final state. Further improved descriptions of nuclear dynamics in the initial and final ground states would imply a quantization of vibrational energies, at least for the most relevant torsional degrees of freedom, and a computation thereby of Franck-Condon factors if we assume that the Born-Oppenheimer approximation remains valid. On longer terms, coupled electron-nuclear dynamical simulations of (e, 2e) experiments should also be considered for quantitatively describing ultra-fast dissociation processes that may be subject to a breakdown of the Born-Oppenheimer approximation. Considering the number of trajectories that one would need to compute for enabling reliable enough statistics, this goal will probably remain beyond reach for a number of years. Meanwhile, effort is required on the experimental side for a better monitoring of important parameters such as the temperature, and the time scale characterizing (e, 2e) electron impact ionization processes.

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