

Orbitals are ubiquitous [1] in the quantum theory of matter. It is well-known that, at the molecular level, motions of electrons can only be statistically described through one-electron waves – the orbitals. For many-electron systems, the consistency of the orbital formalism can only be assessed by comparing various predictions drawn from quantum mechanics with a set of experimental observations. In this context, Electron Momentum Spectroscopy (EMS) [2] has triggered a revolution in our perception of the electronic structure of matter. In contrast with most structural analysis techniques which can only deliver direct information on the *total* electron densities, this technique indeed affords *direct measurements* in momentum space ( $\mathbf{p}$ ) of the electron density associated to a single ionization channel (i.e. an orbital in a one-electron picture), through detailed investigations of the angular dependence of electron impact (e,2e) ionization intensities. The obtained momentum distributions (MDs) are equivalent to structure factors derived as the square of the Fourier Transform of suited orbitals, namely Dyson orbitals [ $g_n(\mathbf{x})$ ], defined as partial overlaps between the initial (neutral) and final (cationic) wavefunctions in an ionization process. EMS enables us therefore to directly assess the intimate relationships that prevail between the configuration ( $\mathbf{r}$ ) and momentum ( $\mathbf{p}$ ) spaces for specific ionization channels related to well-defined electron energy levels.

Valence electron spectra are often qualitatively interpreted according to orbital energies and with the help of familiar one-electron concepts, such as Hartree-Fock molecular orbital theory and Koopmans' theorem [3]. This approach is known to yield significant errors in the assignment of spectral bands as well as to large deviations in the apparent shape of orbitals compared with EMS measurements. Assuming an extension of Koopmans' theorem, a commonly used alternative in the EMS community for coping with electron correlation in the initial ground state wavefunction (shortly, initial state correlation) is Density Functional Theory (DFT) [4]. Kohn-Sham orbitals have been almost systematically used over the last twenty years to analyze the experimental MDs, which they most often remarkably reproduce. However, most currently used gradient corrected functionals are known to yield systematic underestimations of ionization energies by several eV [5-7].

The main drawback of a description of ionization events at the level of Koopmans' theorem is that final state configuration interactions are neglected as well as the dispersion thereby of the ionization intensity over excited electronic (shake-up) configurations of the cation. Note that shake-up bands may borrow a very high fraction of the total ionization intensity [8].

A further considerable difficulty impeding widespread applications of EMS is that many molecules, oligomers or polymers are flexible entities. As variations of the molecular conformation may induce considerable changes in the ionization energies and on the related (e,2e) transition densities, robust enough computations of conformer abundances are essential in reliable analyses of the results of EMS experiments on such systems.

A third difficult issue that can still be hardly handled nowadays pertains to the role played by vibronic coupling interactions and ultrafast nuclear dynamical effects, which may culminate in the form of Coulomb explosion processes when multiple electron vacancies are created. As is shown in the thesis of the candidate [6, 9, 10], electrostatic repulsions in doubly ionized and cyclically strained molecules can be strong enough to result into an ultrafast Coulomb explosion, which may lead to specific fingerprints in EMS experiments.

In the described research, we rely extensively on the so-called third-order algebraic diagrammatic construction scheme [ADC(3)] [11] derived within the framework of one-particle Green's function (1p-GF) theory [12] for calculating valence one-electron and shake-up ionization

states. Within this scheme, the scattering potential is described with the right asymptotics and Dyson orbitals are computed through third order in correlation. ADC(3) enables therefore calculations of ionization energies and Dyson orbitals at a level of accuracy comparable to that of the benchmark multireference single-double configuration-interaction (MR-SDCI) scheme [13] with the advantages of size consistency [14] and of a greater compactness of the secular matrices to diagonalize.

In order to correctly pinpoint the lowest stationary points of the conformationally versatile molecules within the confines of non-relativistic quantum mechanics, the convergence of the conformational energy differences towards the exact solution of the Schrödinger equation are exploited by pairing increasingly complex levels of theory with basis sets of improving quality in a Focal Point Analysis (FPA) [15]. More specifically, highly reliable predictions are achieved [16, 17] within an accuracy of  $\sim 0.1$  kcal mol<sup>-1</sup> by means of well-suited extrapolations to the level of a coupled-cluster treatment along with single, double, and (perturbative) triple excitations [CCSD(T)] in the limit of an asymptotically complete basis set.

Relative conformer abundances were calculated according to Boltzmann thermostatics by means of Gibbs' free energy differences including our best (FPA) estimates for the conformational energy differences, and from statistical partition functions computed beyond the Rigid-Rotor/Harmonic-Oscillator approximation [18].

The conversion of orbital densities to momentum space was carried out by means of the Gaussian Weighted Planar Grid (GW-PG) method of Duffy *et al.* [19], to cope with the limited resolution in momentum space.

In this thesis, we focused on EMS studies of two very opposite kinds of molecular species, namely rigid cage compounds (norbornane [6, 10, 11], norbornene [7], stella-2,6-diene, stella-2,6-dione, bicyclo[2.2.2]octane-2,5-dione and bicyclo[2.2.1]heptane-2,5-dione [8]) and conformationally flexible molecules (*n*-pentane [17], dimethoxymethane [18], 1,3-butadiene [20]). The latter work [20] was motivated by recent interpretations of EMS measurements [21] in striking contradictions with elementary thermodynamics, due to the neglect of the conformational dependence of ionization energies. A detailed study of the electronic structure of biphenyl [22] was also presented using 1p-GF theory and Penning Ionization Electron Spectroscopy (PIES) [23]. With the latter technique, the shape and stereochemistry of molecular orbitals towards an approaching electrophilic species are experimentally amenable through studies of the collision energy dependence of partial ionization cross sections upon impact with a rare-gas atom in a metastable excited state. In further studies on difluoromethane [24] and water [25], we emphasized the limitations of the Hartree-Fock and DFT approaches in analyses of EMS experiments, and demonstrated that ADC(3) Dyson orbitals provide a robust alternative for computing electron MDs.

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