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# Molecular potentials and wave function mapping by high-resolution electron spectroscopy and *ab initio* calculations

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### ABSTRACT

The recent development of high brightness 3<sup>rd</sup> generation soft X-ray sources and high energy resolution electron spectrometers made it possible to accurately trace quantum phenomena associated to the vibrational dynamics in core-excited molecules. The present paper reviews the recent results on mapping of vibrational wave functions and molecular potentials based on electron spectroscopy. We discuss and compare the mapping phenomena in various systems, stressing the advantages of the resonant X-ray scattering for studying of the nuclear dynamics and spectroscopic constants of small molecules. The experimental results discussed in the paper are most often accompanied by state-of-the-art *ab initio* calculations allowing for a deeper understanding of the quantum effects. Besides its fundamental interest, the vibrational wave function mapping is shown to be useful for the analysis of core- and valence-excited molecular states based on the reflection principle.

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## 1. Introduction

One of the fundamental concepts of modern chemical physics and quantum chemistry is the Born–Oppenheimer (BO) approximation, which allows considerable simplification of *ab initio* calculations and of the analysis of experimental molecular spectroscopy data. The BO approximation assumes that the total molecular wave function may be represented as a product of electronic and nuclear wave functions, thus decoupling the electronic and nuclear degrees of freedom. This wave function splitting allows one to employ a two-step approach. In the first step, one solves an electronic Schrödinger equation at fixed nuclei positions. The dependence of the electronic energy on nuclei's positions forms a potential energy surface or, in the one-dimensional case, a potential energy curve (PEC). In the second step, the nuclear dynamics is determined from the solution of the nuclear Schrödinger equation with a Hamiltonian which includes the nuclear kinetic energy and the electronic energy of a particular electronic state. This step may additionally involve separation of the vibrational, rotational

and translational degrees of freedom. In the high-energy electron spectroscopy studies presented here, the translational and rotational motions have only minor effects observed in the spectral broadening of the lines [1,2], while the vibrational motion plays a crucial role in the spectra formation. The eigenfunctions of the vibrational Hamiltonian – the vibrational wave functions (VWFs) – and the PECs are well known quantum concepts, which are widely used in the interpretation of the modern ultrahigh resolution spectroscopic data tracing complex molecular dynamics. However, the question arises how these quantum concepts are related to the experimental observables, and if they can be mapped directly from the measurements?

The experimental scheme to address this question was proposed almost twenty years ago based on the theoretical prediction of the vibrational wave function mapping phenomena in the framework of the resonant X-ray scattering theory applied to the excitation/decay processes involving dissociative final states [3]. Indeed, the resonant scattering cross section was shown to be proportional to the square of the wave function of the vibrational sublevel involved in the scattering process [3–5], thus mapping its spatial distribution and the nodal structure according to the reflection principle [6]. In spite of the recent progress in vibrational motion tracking by pump–probe approaches using ultrashort laser pulses [7–11], only very few experimental studies have tried to address

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this phenomenon in resonant photoemission (RPE) [12–18]. The main obstacles for the observation of the VWF mapping is a collective excitation of the vibrational sublevels when the photon bandwidth and lifetime broadening are broader than the vibrational quanta of the core-excited electronic state, as well as a high density of the final electronic states. To overcome this, one has to use an X-ray photon bandwidth smaller than the lifetime broadening (the so-called resonant Auger–Raman conditions [19,20]), and record ultrahigh resolution spectra allowing for an accurate state assignment. Such experimental conditions became recently available at the 3<sup>rd</sup> generation synchrotron X-ray radiation sources with the help of highly resolving instruments, and allowed for instance to establish new concepts [21] or to extract geometric information about core-excited states from RPE spectra of simple molecules [22,23]. Besides its fundamental interest, the experimental recording of the shapes of VWFs combined with state-of-the-art *ab initio* simulations allows analyzing the shapes of the core-excited and final-state potentials and deriving some important molecular parameters, such as the slope of the dissociative states PEC, the classical turning points of the bound PEC, their spectroscopic constants and the electronic transition energies.

In the present paper we summarize several recent results describing the PEC and VWF mapping in the framework of the high resolution electron spectroscopy. In particular, we focused on the observation of the VWF mapping in the RPE spectra of CO [12], N<sub>2</sub> [13,17,18], KF [15], BF<sub>3</sub> [14], and in the photoelectron–Auger electron coincidence spectrum of CH<sub>4</sub> [16]. The use of the recorded wavefunctions for the mapping of the potential energy curves of the core-excited [14] and final electronic states [14,16–18] are also discussed. In most of these cases the experimental results were analyzed with the help of *ab initio* simulations allowing to get a deeper insight into the studied quantum effects.

The paper is organized as follows. In Section 2, we give a brief theoretical description of the mapping phenomena manifestation on dissociative and bound molecular potentials. In Section 3, we summarize the experimental results showing the VWF mapping in the framework of the resonant photoelectron spectroscopy. In Section 4, we are discussing recently proposed techniques for molecular potentials reconstruction based on VWF reflection principle and *ab initio* calculations. We draw our conclusions in Section 5.

## 2. Vibrational wave function mapping phenomena in resonant X-ray scattering

The resonant photoemission process transfers the neutral molecule from its ground state to a number of excited electronic states of the singly ionized molecule with the emission of an electron of energy  $E$  from the valence orbitals. This process is enhanced when the photon frequency  $\omega$  is tuned in resonance with a core-excited state, and the core electron is promoted to an unoccupied valence molecular orbital (see Fig. 1(a)). For an accurate simulation of the RPE spectra the time-dependent solution of the Schrödinger equation has to be employed [18]. However, the principle of VWF mapping phenomena can be explained based on the time-independent description of the scattering process [3]. Using the generalized Kramers–Heisenberg approach the RPE cross section reads in a general case [24] (in atomic units):

$$\sigma_0(E, \omega) \propto \sum_f |F_f|^2 \delta(\omega - E - \omega_{fg}), \quad F_f = \sum_i \frac{\langle v_f | Q | v_i \rangle \langle v_i | V | v_g \rangle}{\omega - \omega_{ig} + i\Gamma_i}. \quad (1)$$

Here we neglected the lifetime broadening of the final electronic state, which is much smaller than that of the intermediate

(core-excited) state,  $\Gamma_i$ .  $\delta$  is Dirac delta-function,  $V$  is the electronic matrix element of the dipole interaction of the incoming X-ray photons with the molecule,  $Q$  is the Coulomb interaction matrix element describing the Auger decay,  $\omega_{jk} = \varepsilon_j - \varepsilon_k$  ( $j, k = g, i, f$ ),  $\varepsilon_j$  and  $v_j$  ( $j = g, i, f$ ) are the eigenvalues and the eigenfunctions, respectively, of the nuclear Hamiltonian of the ground  $g$ , intermediate  $i$ , and final  $f$  electronic states.

In the case where the final electronic state is dissociative, the sum over final vibrational sublevels  $f$  in (1) should be replaced by the integration over energy of the final-state continuum,  $E_f$ . Let us linearly expand the final-state potential near the equilibrium position of the core-excited state  $R_0$  as  $E_f(R) = E_f(R_0) - (R - R_0)U_f$ , where  $R$  is the internuclear distance and  $U_f$  is the interatomic force at  $R_0$ . In the limit of very short de Broglie wavelength, the continuum wave function of the final electronic state can be approximated by the Delta function at the classical turning point  $\delta(R - R_t(E))$  [25]. This very simple model allows to see immediately the physics behinds the VWF mapping phenomena. Indeed, the integration over  $R$  and  $E_f$  are easily performed in that case, and the cross section (1) becomes:

$$\sigma_0(E, \omega) = \left| \sum_i A_i \frac{v_i(R_t)}{\omega - \omega_{ig} + i\Gamma_i} \right|^2, \quad A_i \propto VQ \langle v_i | v_g \rangle, \quad R_t(E) = R_0 + \frac{(\omega - E - \omega_{fg}(R_0))}{U_f}. \quad (2)$$

In (2) we assumed the validity of the Franck–Condon approximation, where the transition matrix elements  $V$  and  $Q$  are independent on  $R$ . Let us note that the calculations using a rather accurate approximation of the continuum wave functions by Airy functions [26] result in qualitatively the same equation for the shape of the RPE profile [3]. This can be understood from the simple consideration of Airy functions plotted in the central panel of Fig. 1(a). Indeed, the main contribution to the overlap integrals is given by the first main peak of the continuum function, while the rest vanishes due to its fast oscillatory behavior. In the case where photon bandwidth is smaller than the lifetime broadening of the core-excited state one can tune the X-ray energy in resonance with a single vibrational sublevel  $i_0$  of the core-excited state. Eq. (2) clearly shows that in this case the RPE cross section

$$\sigma_0(E, \omega = \omega_{i_0g}) \propto |v_{i_0}(R_t(E))|^2 \quad (3)$$

reflects the nodal structure of the core-excited state VWF: the zeros of the VWF are mapped one to one by the minima of the RPE profile. This phenomenon has a rather simple geometrical interpretation based on the reflection principle [6] as illustrated in Fig. 1(b). Although it is well known in the case of photodissociation dynamics [10,25], where the ground state vibrational wavefunctions are mapped, it was not observed until recently in the RPE case, which allows recording the VWF of the highly excited core-hole states with extremely short (few femtoseconds) lifetime. Let us note that reflection of the wavefunction is not exact but affected by the shape of the final-state potential. Apparently, the slope of the final-state PEC in the Franck–Condon region affects the energy interval between the spectral features reflecting the nodal structure of the core-excited state VWF. When the shape of the final-state potential is known, one can apply a reconstruction procedure in order to get the correct shape of the VWF.

Beyond the original prediction, the core-excited state VWF can be also mapped using bound final states. When the minimum of the potential is shifted toward larger bond lengths compared to the right classical turning point of the core-excited state wave packet the RPE cross section carries direct information about the nodal structure of the core-excited state VWF [18]. As illustrated in Fig. 1(b) the left classical turning point (short bond length) of the

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