Dependence of the angular distributions in photoionization of $H_2^+$ on the initial and final state representation

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Abstract. We present a detailed study of the angular distribution in photoionization of $H_2^+$ in different geometrical arrangements between the internuclear axis and the polarization vector. We compare the results of an exact calculations with those obtained employing approximate initial and final state wave functions. We find large and unexpected differences if we employ the 2C or exact final state continuum wave functions with the same initial state. We find also that the results depend on the accuracy of the initial bound state. As the quality of the final state is improved we obtain results in closer agreement with the exact angular distributions.

1. Introduction
The spectra of emitted electrons from atoms and molecules induced by charged particle or photon impact allows to study in detail the multiple electron continua [1]. For charged particle impact the emitted electrons move freely in the presence of the scattered projectile and the residual target potentials. In the case of molecular targets a further complication arises because the corresponding potential depends on its multicenter geometry. Thus, the angular and energy distributions give information about the interaction between the emitted electrons, of their interaction with the target potential and, for charged particles, of the distortion produced by the projectile Coulomb potential.

While it is possible to calculate accurately the bound states of atoms and molecules, employing for example the Hartree-Fock or Density Functional Methods, there are no equivalent methods for the continuum. Recent applications of B-splines look quite promising, although the method has been applied only for photoionization [2]. Most calculations performed up to now approximate the multiple particle continuum by products of two-body continuum states (for review articles see [1]). The validity of this perturbative method is usually determined by comparing the results with experimental data. In most cases this method is the only one that can be effectively implemented for the computation of cross sections. It is therefore quite rewarding that good agreement is obtained with the experimental data. There is however recent evidence that this method fails when the comparison with experiments is performed in greater detail.
In recent experiments the electron emission spectra was measured in collisions between highly charged ions and H$_2$ [3]. The ratio of these cross sections with the corresponding ones for H showed oscillations which were interpreted as Young-type interferences due to the coherent emission from the two atoms forming the molecular target. Theoretical calculations, employing the effective center approximation for the final state, show a very good qualitative agreement with the experimental data [4]. The calculations fail however to reproduce the dependence of the oscillation frequency on the emission angle [4] and in some cases it underestimates the amplitude of the oscillation [5]. The same kind of discrepancy appears in the case of electron impact [6]. In these calculations the initial state is represented by a linear combination of two atomic orbitals. The transition matrix can then be expressed as the sum of two transition matrices which correspond to the emission from each effective hydrogen atom forming the molecule. In the effective center approximation the final continuum state in each of these contributions is approximated by that of the corresponding atom. Therefore the effect of the other atomic center of the molecule is neglected in both terms and the final state is not represented by a full two-center wave function corresponding to the emitted electron in the field of the residual molecular target. It is important therefore to analyze the sensitivity of the results to the description of the final state as a possible source for the discrepancies between theory and experiment.

For this purpose it is desirable to choose a system in which the cross sections can be computed exactly. This provides a benchmark with which to compare the different approximations. A system which is well suited for this purpose is the photoionization of H$_2^+$. This system has two advantages: the bound and continuum states of the target, and therefore the transition matrix, can be computed exactly within the dipole approximation and there is no need to worry about the momentum transfer as in the case of massive particles. In a series of recent works, photoelectron emission from H$_2^+$ has been considered in some detail [7, 8, 9, 10, 11, 12]. These studies indicate that some of the accepted methods to represent the continuum states must be analyzed in more detail. Atomic units will used except were otherwise stated.

2. Representations of the H$_2^+$ initial and final states

We consider the one-electron hydrogen molecular ion formed by nuclei A and B which are separated by the internuclear distance $R$. The molecular and laboratory coordinate systems are described in figure 1. All the results presented here are given in the molecular frame. We employ the Bohr-Oppenheimer approximation and assume that the nuclei in the molecule are at a fixed distance. We will consider the case of linear polarization, characterized by the polarization vector $\hat{z}$, and employ the dipole approximation.

The photoionization of H$_2^+$ was first studied by Cohen and Fano [13]. These authors employed a linear combination of atomic orbitals (LCAO) for the initial state wave function:

$$\psi_1(r) = [2(1 + S)]^{-1/2} [\varphi(r_A) + \varphi(r_B)]$$

where $\varphi(r_A)$ and $\varphi(r_B)$ are hydrogenic wave functions centered on nuclei A and B respectively. The ejected electron wave function was approximated by a plane wave (PW):

$$\psi_{PW}(k_e, r) = (2\pi)^{-3/2} e^{ik_e \cdot r}$$

where $k_e$ is the emitted electron momentum. This simple method allowed Cohen and Fano [13] to predict Young-type oscillations in the photoelectron spectra from H$_2^+$ due to the coherent emission from the two atoms in the molecule. This model was latter improved by Walter and Briggs [14] who employed a 2C continuum wave function for the final state:

$$\psi_{2C}(k_e, r) = \psi_{PW} N(\alpha)_1 F_1(i\alpha, 1, -i[k_e r_A + k_e \cdot r_A]) N(\alpha)_1 F_1(i\alpha, 1, -i[k_e r_B + k_e \cdot r_B])$$
where $\alpha = -1/k_e$, $N(\alpha)$ is a normalization factor and \(_1F_1\) the confluent hypergeometric function. The calculations with the 2C wave function for 10 eV photoelectron energy showed important discrepancies in the angular distributions with respect to the results obtained with the PW approximation. For example, the PW calculations predicted that the angular distributions are oriented in the direction of the polarization vector while with the 2C approximation they are oriented along the internuclear axis. Moreover, the PW angular distributions show always a $p$-wave like behavior while the 2C calculations show structures for $\Theta_R = 60^\circ$ and $90^\circ$ which are clear indication of additional $f$-wave contributions. Since the 2C wave function gives a better representation of the continuum states it is expected that the results obtained with it are more accurate. However, Foster et al [10] noted that the 2C wave function has some good intrinsic properties but also some basic deficiencies. It verifies the correct asymptotic conditions at high $k_e$, but it can not represent the united atom limit ($R = 0$) and is not gauge invariant. We can expect therefore that the results from this model will be closer to the exact results and will agree with them at high values of $k_e$. We don’t know however how good it is in a large range of electron momenta from threshold to the asymptotic values. It is therefore worthwhile to compare the 2C results with even better representations of the final state and with exact calculations to answer these questions.

To study the limitations of the 2C wave function Della Picca and coworkers [8] employed the exact final state obtained by solving numerically the Schrödinger equation in prolate spheroidal coordinates $(\xi, \eta, \phi)$:

$$\psi(k_e, r) = \frac{4\pi}{(2\pi)^{3/2}} \sum_{m=-\infty}^{\infty} \frac{1}{i} \sum_{l=|m|}^{\infty} \mathcal{Y}_{lm}(c, \cos \theta_e, \phi_e) \mathcal{Y}_{lm}(c, \eta, \phi) X_{ml}(c, \xi) e^{-i\Delta_{ml}}$$

where $c = k_e R/2$, $\mathcal{Y}_{lm}$ are the spheroidal harmonics, $X_{ml}$ the quasi-radial wave functions and $\Delta_{ml}$ the phase shift [15].

3. Results and Discussion

For simplicity we consider here the coplanar geometry where the internuclear axis, the polarization vector and the ejected electron momentum are all on the same plane. We consider
Figure 2. \( \text{H}_2^+ \) molecular frame photoionization differential cross section for 10 eV electron energy and \( \Theta_R = 0^\circ, 30^\circ, 60^\circ, 90^\circ \). Solid line: present calculations with exact final state; dashed line: 2C calculations from [10]. The 2C results for \( \Theta_R = 0^\circ \) and \( 30^\circ \) have been divided by 100 and 10 respectively.

The previous calculations employ a very simple approximation for the initial state. Even though the exact final state is employed, the calculations may not be accurate enough. The use of approximate wave function has also the consequence that the calculations are not gauge invariant. To test the accuracy of this calculation we compare them with calculations employing the exact initial and final wave functions. These calculations are exact within the dipole...
approximation and therefore gauge invariant. In these calculations we check the accuracy of the results by calculating the cross sections both in the length and velocity gauge and find in all cases the same values.

The results are presented in figure 3. We note immediately that the angular distributions are very much the same except at $30^\circ$. Also the results with the LCAO initial state give larger values of the differential cross sections at smaller angles. These discrepancies can be understood from the transition matrix (see equation (5)). When the molecule is oriented parallel or perpendicular to the polarization vector, only $\sigma \rightarrow \sigma$ and $\sigma \rightarrow \pi$ transitions are allowed respectively. For other angles the angular distribution is determined by the coherent sum of these two type of transitions. The $\sigma \rightarrow \sigma$ and $\sigma \rightarrow \pi$ electronic dipole transition elements are complex quantities and therefore their coherent sum depends on their magnitude and phase, which are determined by the weights of the partial waves. The different angular distributions at $30^\circ$ are therefore due to the different values and coupling of the $\sigma \rightarrow \sigma$ and $\sigma \rightarrow \pi$ transition amplitudes. With the LCAO initial state the calculations overestimate the contribution from $\sigma \rightarrow \sigma$ transitions at small angles, particularly that of the $f$-wave. Also this explains why these results are larger than the exact ones in the parallel arrangement. Finally, we note that there is no propensity rule for alignment of the angular distribution by either the internuclear axis or the polarization vector. As recently shown by Della Picca et al [9] this statement is valid at all photoelectron energies. At low values only a few partial waves contribute but anyhow, as seen from figure 3, there is no orientation effect due to the coherent mixing between $\sigma \rightarrow \sigma$ and $\sigma \rightarrow \pi$ transition amplitudes. As the photoelectron energy increases many more partial waves contribute, large interference effects appear, and thus there is also no alignment of the angular distribution.

4. Conclusions
In conclusion we have shown that the calculations of photoelectron spectra are very sensitive to the wave functions of the initial and final states employed. By using the exact final state wave function we have shown that we obtain completely different results from those obtained

Figure 3. Same as figure 2. Solid line: present calculations with LCAO initial state and exact final state; dot-dashed line: present calculations employing exact initial and final states.
previously with the well known 2C approximation. The comparison with exact calculations of the transition matrix shows that the results are also sensitive to the quality of the initial state. The $\sigma \rightarrow \sigma$ and $\sigma \rightarrow \pi$ electronic dipole transition elements depend on the initial and final states employed in the calculation, and therefore the weights of the different partial waves and the coupling between these channels is very sensitive to these states. Differences in the calculated values of the weights result in large differences in the angular distributions which depend strongly on the partial wave contribution. The exact calculations and the results with exact final wave function do not show any alignment with either the internuclear axis or the polarization vector.

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