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Interferences in the photoelectron spectrum of H_2^+ molecules at high energy

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Abstract

We present a theoretical study of ground state H_2^+ ionization by photons of a few hundreds of eV. Bound and continuum states are obtained by using B-spline basis functions. As predicted by Cohen and Fano [H.D. Cohen, U. Fano, Phys. Rev. 150 (1966) 30], the calculated photoelectron spectrum reveals the existence of interference effects that result from the coherent emission in the presence of the two nuclei. We show, however, that one of the basic assumption of the Cohen–Fano model, namely, the validity of the LCAO approximation to describe the initial ground state or the free wave description of the ejected electron, is not fulfilled, which leads to an "anomalous" oscillatory behavior not pointed out in previous works.

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1. Introduction

The H_2^+ ion is the usual starting point to study more complicated diatomic molecules. Firstly, because exact numerical solutions of the electronic Schrödinger equation are available through the use of prolate spheroidal coordinates [1]. Secondly, because problems related to the multi-center nature of molecules may be investigated without the complexity introduced by electron correlation in multi-electronic systems. These features make H_2^+ an excellent candidate to get a deep insight into dynamical problems involving the ionization continuum as, e.g., photoionization. Cohen and Fano [2] (CF) predicted that the spectrum of photoelectrons emerging from diatomic molecules is modulated by interferences coming from the coherent emission from both molecular centers. This prediction is based on three basic assumptions: (i) ionization is basically a *one*-electron process, (ii) the initially occupied molecular orbitals are well described in the LCAO (Linear Combination of Atomic Orbitals) approximation (e.g., in the H_2^+ and H_2 cases, $\psi_g \sim 1s_A + 1s_B$, where $1s_A$ and $1s_B$ are atomic orbitals centred in nucleus A and B, respectively) and (iii) the ionized electron is well described by a single-center spherical or plane wave. Using these simple ingredients, CF showed that, for H_2^+, the total photoionization cross sections (TPCS) are given by the analytical form

$$\sigma = \frac{\sigma_H(Z^*)[1 + \sin(k_e R)/(k_e R)]}{1 + S}, \tag{1}$$

where σ_H is the TPCS of a hydrogen atom with effective charge Z^*, R is the equilibrium internuclear distance, S is the overlap between $1s_A$ and $1s_B$, and k_e is the electron wave vector. This formula shows the typical oscillatory behavior associated with interferences. CF gave a tentative explanation for the presence of structures in the form of undulations superimposed to the monotonic decrease of the TPCS of diatomic molecules, specially nitrogen and oxygen. Moreover, they suggested that the shoulder of an undulation was related to the onset of ionizing transitions to states of higher orbital momentum than those involved at lower photon energies. To test their hypothesis, CF recommended that further calculations were carried on. In particular, they called the attention to H_2^+ owing to the

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fact that performing accurate computations of the TPCS was already possible in those days. Thus, two years later, Bates and Opik [3] performed the first "exact" calculations on H_2^+ for energies of ejection up to 8 a.u., but they found no undulations in the photoionization cross section. Later, Richards and Larkins [4] extended these calculations to partial photoionization cross sections, continuum phase shifts and angular distributions of photoelectrons using essentially a similar "exact" one-electron treatment in spheroidal coordinates. Their results covered the intervals $[0, 2]$ a.u. in steps of $\Delta = 0.2$ a.u. and $[2, 6]$ a.u. in steps of $\Delta = 1$ a.u. In addition, they provided results for the two additional energies 10 and 20 a.u. Brosolo and Decleva [5] developed a one-center approximation with a radial basis of B-splines (hereafter, work I). Photoionization partial cross sections, phase shifts as well as asymmetry parameters were computed up to photoelectron energies of 8 a.u. every 0.1 a.u. Later, these computations were improved by including a larger number of angular momenta (work II) [6]. Finally, an LCAO expansion in a B-spline basis with $l_{\max} = 5$ was developed (work III) [7]. Due to the limited energy range investigated in these previous works, no additional indication about the existence of undulations (or not) in the photoionization cross section was reported.

Very recently, the subject of interferences in H_2^+ photoionization at high photon energies has been revisited by Walter and Briggs [8] at a more qualitative level. Photoionization of H_2^+ as well as single photon double ionization of H_2 have been theoretically analyzed by these authors following the ideas of CF [2]. In the case of H_2^+, they have employed a simple LCAO approximation to describe the initial molecular bound state as in the work of CF but an improvement in the description of the final continuum function is performed: instead of a plane wave description for the ejected electron, a product of two two-body Coulomb distortion factors is used (a 2C wave function). An interesting conclusion is that the calculated cross sections obtained with 2C wave functions and plane waves strongly disagree from each other for specific molecular orientations, whereas cross sections integrated over all molecular orientations are quite similar for either choice of the final continuum state [8]. To our knowledge, the kinds of interferences predicted by CF in H_2^+ have not been observed so far in photoionization experiments. However, recent measurements [10] on single ionization of H_2 molecules by impact of fast heavy ions have shown interference patterns similar to those predicted by CF. The latter observations have been supported by effective one-electron continuum distorted wave calculations [11] in which the initial molecular orbital is described by a LCAO. Analogous interference patterns have been predicted [12] and measured [13] for electron impact on H_2 molecules using a similar description of the initial molecular orbital.

It seems therefore appropriate to investigate in greater detail if similar interferences exist in H_2^+ photoionization, for which the original CF model was introduced and Eq. (1) was deduced. In this work, we have evaluated TPCS and partial photoionization cross sections (PPCS) of H_2^+ for photon energies up to 25 a.u. (∼680 eV). We have used the computer programs developed by Sánchez and Martín [14,15] to describe the molecular states of H_2^+ in a basis of B-splines [16]. This work is complementary to our recent work on interference effects in photoionization of the H_2 molecule [9] in which the same B-splines techniques were employed. In the latter work we have found that our calculations for H_2 up to 20 a.u. lead to undulations as those predicted by CF, but important deviations are observed at low photon energies. Atomic units are used throughout unless otherwise stated.

2. Theory

As we are not interested in the vibrational analysis of the H_2^+ ion, we will work in the fixed nuclei approximation [15], i.e., we will completely neglect the nuclear degrees of freedom. As explained in previous works [14,16], this is a reasonable approximation for total cross sections, except very close to the ionization threshold. This is because ionization is much faster than the typical vibrational or rotational periods of the molecule (except for the case just mentioned). We use the dipole approximation, average among all possible molecular orientations and sum over all possible final vibrational states. Thus, the total photoionization cross section is given by

$$\sigma(\omega) = \frac{4\pi^2\omega}{3c} \sum_{lm} \sum_{p} \left| \langle \Psi_g | \mathbf{e}_p \cdot \mathbf{D} | \Psi^+_{lmE} \rangle \right|^2, \tag{2}$$

where ω is the photon energy, c is the speed of light, $\mathbf{e}_p$ is the polarization vector along the p direction, $\mathbf{D}$ is the dipole operator (in its length or velocity form), Ψ_g is the initial ground state of H_2^+ at the equilibrium distance $R = 2$ a.u. (with energy E_g), Ψ^+_{lmE} is the final continuum state of H_2^+ at $R = 2$ a.u. with the usual outgoing boundary conditions, l is the angular momentum of the ejected electron, m its projection along the molecular axis and $E = \hbar\omega + E_g$. Since the ground state of H_2^+ has $^2\Sigma_g^+$ symmetry, the dipole selection rule implies that only continuum states of $^2\Sigma_u^+$ and $^2\Pi_u$ symmetries can be populated.

3. Results

We have computed TPCS in both length and velocity gauges for H_2^+ molecules in their ground electronic state $^2\Sigma_g^+$. We have employed B-splines of order eight which are defined on a linear knot sequence contained in a box of 60 a.u. of length. For the ground state of H_2^+, we have included values of the angular momentum up to $l = 20$ and a set of 280 B-splines per l. For the final continuum states, we have included values of l up to $l = 7$ and 280 B-splines per l-value. We have checked that discrepancies between TPCSs obtained in length and velocity gauges are always less than 3%. For final $^2\Pi_u$ states, discrepancies are less than 5% whereas for $^2\Sigma_u^+$ states they are less than 3–10%, the largest error corresponding to the larger energies presented in this work. In the latter case, the largest errors are observed for $l = 5$ and $l = 7$, especially at the higher photon energies. In what follows, we only show results obtained in the velocity gauge since, as usual, they are expected to be better converged.

In Fig. 1 we present the TPCS of H_2^+ as a function of photon energy. Contributions coming from the $^2\Sigma_u^+$ and $^2\Pi_u$ symme-