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Sturmian Approach to Single Photoionization of CH_4

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Abstract Single photoionization cross sections for two different ground state orbitals of the molecule CH_4 are presented. An angular averaged molecular model potential is used to represent the interaction of the ionized electrons, whose continuum wave functions are calculated within a generalized Sturmian functions approach.

The quantal description of ionization processes in molecular systems (even in simple ones) is highly complex due to the multicenter nature of the electronic wave functions and to the large number of particles (electrons and nuclei). To make calculations tractable, one necessarily needs to make a number of assumptions and simplifications. One approximation used successfully in the past indicates that the molecular structure can be described in the *self-consistent field* approach [1,2] which uses a spherically symmetric potential for individual electrons. Generally, this leads to a reasonable agreement between calculated and experimental cross sections, in particular when the molecular systems possess a high degree of symmetry, as in the case of CH_4 [3]. Another useful approximation is the one-center expansion (OCE) where all the electronic wave functions are referred to one common origin located, typically, in the heavy nucleus [2,4,5]. In the case of CH_4, since the heavy nucleus is located in the center of mass of the molecule, the OCE is particularly adequate [2,6]. In this contribution we shall make these two approximations. On top of working with model potentials, we shall use—as a first step—central potentials and therefore reduce the problem to one active electron problem. The main purpose of the present investigation is to apply the generalized Sturmian functions (GSF) method [7,8] to study single photoionization, here illustrated with the example of CH_4. Once the use of GSF for molecular scattering states is mastered, further steps will include taking more realistic descriptions: one active electron but non-central potentials (including exchange terms), and finally *all* active electrons. Another aim of this investigation is to compare the procedures of averaging the potential with respect to averaging the calculated cross sections over all possible orientations.

Let H_0 be the unperturbed Hamiltonian of the molecule containing, as a first step, a central model potential. To study photoionization, we want to solve the time-independent Schrödinger equation (TISE) in a first order perturbation theory, with the dipolar operator in the velocity gauge (atomic units are used throughout)

$$(\omega_1 - \omega - H_0)\,\Phi^{(1)}(\mathbf{r},\omega) = -i\hat{z}\cdot\nabla\Phi^{(0)}(\mathbf{r})\,, \tag{1}$$

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where ω_1 is the energy of the photoelectron, $\Phi^{(1)}(\mathbf{r}, \omega)$ is the first order scattering wave function, $\Phi^{(0)}(\mathbf{r})$ is the initial ground state (solution of H_0), and ω is the energy of the photon (linearly polarized along the z axis) absorbed by the molecule.

The ionized electron is assumed to interact with an angular averaged molecular potential $U_i(r)$ which can be obtained as follows (see Ref. [9], where it has been applied successfully for the study of collisions of ions with molecules). We start with the independent particle model, considering one active-electron (coordinate $\mathbf{r}$) placed in a molecular orbital (MO) i of the ground state, with the corresponding wave function $\varphi_i(\mathbf{r})$ given, for example, by Moccia [2]. The molecular model potential then reads

$$V_i(\mathbf{r}) = -\sum_{n=1}^{M} \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} + \sum_{j=1}^{N_{mo}} N_{ij} \int d\mathbf{r}' \frac{\left|\varphi_j(\mathbf{r}')\right|^2}{|\mathbf{r} - \mathbf{r}'|}, \tag{2}$$

where M is the number of nuclei (placed at coordinates $\mathbf{R}_n$), N_{mo} is the number of MOs and $N_{ij} = 2 - \delta_{ij}$ (δ is the Kronecker symbol). The first term of (2) gives the interaction of the electron in the MO i with each nucleus. The second term is the electrostatic potential between the electron with other electrons located in different MOs; since this term includes, through the electronic densities, wave functions containing the correlation provided by the Hartree-Fock approach, it provides an overall correlated treatment of the system [2,9]. As this model potential is designed to study ionization with the molecule as a parent ion with a free electron with high energy, the exchange potential terms are excluded as a first approximation. The MOs studied here, within the one-active electron approximation, correspond to $2a_1$ and $1t_2$: they are external electrons and therefore the most active in the molecule [2,10]. The corresponding initial wave functions $\Phi^{(0)}(\mathbf{r})$ are taken from Moccia [2]: they include full correlation from a Hartree-Fock approach. It is also assumed that the ionization of these electrons do not involve additional processes that could modify substantially the electronic structure of the molecule after emitting.

The angular averaged molecular potential $U_i(r)$ can be obtained from (2), following

$$U_i(r) = \frac{1}{4\pi} \int_{4\pi} d\hat{r}\, V_i(\mathbf{r}), \tag{3}$$

which gives a central potential used to solve the TISE (1). The effective charge (the potential times r) associated with the non-averaged $V_i(\mathbf{r})$ (Eq. (2)) and with the averaged $U_i(r)$ (Eq. (3)) molecular potentials for the $1t_2$ MO of CH_4 are compared in Fig. 1a. We can see that both potentials reach asymptotically a charge -1, as it should be to study single ionization. The angular averaged potential $U_i(r)$ contains the many-body effects included through the different terms of (2). This approach, which simplifies substantially the problem, is similar to that used in studies of electron-molecule collisions (see, for example, [12**?** –14] and references therein), in the sense that the problem is reduced to a one active electron problem. This is true for small molecules such as H_2O and CH_4, but even more for larger ones such as cytosine [15] or thymine [16]. The simplified potential (3) is certainly not appropriate enough to evaluate the molecular spectrum, but provides a first, reasonable, description for constructing scattering states which are notoriously more difficult to deal with.

The final continuum radial wave function satisfying the driven equation (1) is expanded in a set of one-electron GSF, with correct asymptotic behavior (asymptotic charge 1) [7,8]. The transition amplitude, and therefrom the photoionization cross section, is directly extracted from the asymptotic limit of the scattering solution [7]. Our cross section calculations for the $2a_1$ and $1t_2$ MOs are shown in Fig. 1b, and are compared with those performed by Kilcoyne et al. [17], calculated using the ground state inversion potential method/diffraction (GIPM/D) theory. In spite of our rather crude approximations, we find a reasonable good agreement (of the same kind observed in other theoretical calculations for similar molecular systems, see e.g. [18]). We should emphasize that the GSF used in this work are simple one-electron basis related to a central potential: their linear combination demonstrate to work efficiently to study the ionization of a molecule. A more accurate basis could be a linear combination of many molecular states, constructed with molecular Sturmian functions, extending thus the Hartree-Fock approach. Such an improvement is currently under study, and is part of the follow up of the present work. In spite of this, as a first approximation, the use of GSF for the study of ionization of molecular systems looks very promising. We should recall that there are not many approaches providing molecular states with scattering behavior (pure outgoing) [12,13]; this contribution aimed to show that the use of GSF constitutes an alternative viable method.

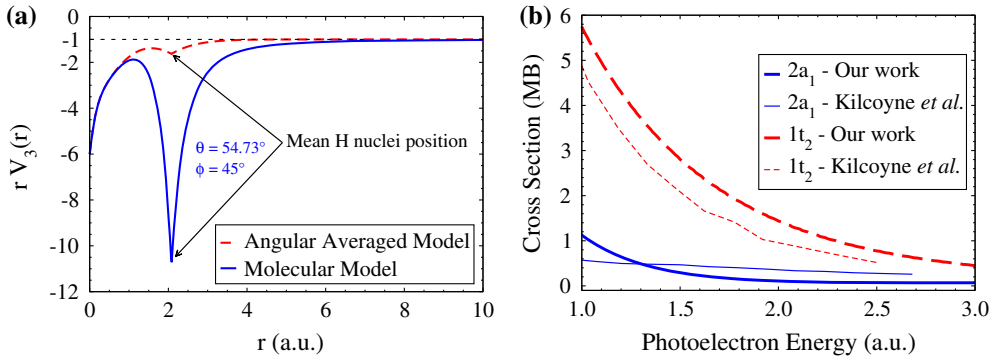

Fig. 1 (Color online). **a** Effective charge (molecular model potential multiplied by r) for the $1t_2$ MO of CH_4: non-averaged (V_i (**r**), Eq. (2)) at indicated angles (*blue*, *solid*) and angular averaged (U_i (r), Eq. (3)), (*red*, *dashed*); **b** Calculated photoionization cross sections for two different initial MOs of CH_4: $2a_1$ (*blue*, *solid line*) and $1t_2$ (*red*, *dashed line*). Our results (*thick curves*) are compared with those of Kilcoyne et al. [17] (*thin curves*), calculated by the GIPM/D theory

The present study allowed us to test the effect of averaging the molecular potential before the evaluation of the cross sections. In the past, many attempts were performed to calculate the cross sections from an average of all the angular orientations of the molecule (see [14] and references therein), but this kind of calculations are often too demanding in terms of computational resources. For that reason the use of angular averaged potentials is common in (e, $2e$) calculations [19], and gives excellent results in the case of the study of symmetric MOs.

As a further step, to be presented soon elsewhere, we will use a more realistic model potential, as Eq. (2), which will include explicit interactions with all the nuclei and the other electrons. This will lead to an angularly coupled set of equations, that could include (explicitly or implicitly) the interaction with other electrons, i.e. implying a full treatment of the system. Other scattering processes such as double ionization will then also be considered.

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