

Theoretical methods for the calculation of the multiphoton ionisation cross-section of atoms and molecules

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Abstract. Some of the available theoretical methods to compute the two-photon ionisation cross-section of many-electron systems are reviewed. In particular the problems concerning the computation of (i) reliable approximations for the transition matrix elements and the excitation energies; and (ii) accurate results pertaining to the electronic continuum by the use of L^2 basis functions are considered.

Keywords. Multiphoton ionisation; theoretical methods; reliable approximations; transition matrix elements.

1. Introduction

In the theoretical interpretation of multiphoton processes a pivotal role is played by the transition matrix elements between ground–excited and excited–excited states of the system considered. In this paper I will confine my considerations to the calculational problems concerning transitions that are essentially electronic in character. In addition, since electron emission is one of the most efficient decay mechanisms for atoms or molecules excited above the ionisation limit (which makes photoionisation cross-section measurement one of the most sensitive probes to study the photoabsorption processes in atoms and molecules), attention will be focused on the available methods to compute the two-photon ionisation cross-section. In order to not encumber the presentation with too many details the present considerations will imply the following simplifications:

- Frozen nuclei approximation (or vertical transition approximation, VTA. For comparison with gas phase experiments the calculated quantities will be orientationally averaged).
- The dipole approximation and the lowest order perturbation theory (LOPT).
- Photon energies sufficiently far from any excitation of the system (off intermediate state resonances).

Adopting the above simplifications and with a_0 and t_0 the atomic units (a.u.) of length and time, and α the fine structure constant, the quantity of interest here is (Cacelli *et al* 1990)

$$\frac{\partial \sigma_{j_e, k_e + \{0\}}^{(2)}(\omega_1, \mu_1, \omega_2, \mu_2; \beta)}{\partial \Omega_{\hat{k}_e}} = (2\pi)^3 a_0^4 t_0 \alpha^2 \omega_1^g \omega_2^g \times \\ \times \sum_{J, M} \sum_L \sum_{j_1, j_2} A_{\mu_1, \mu_2}(L, J, M; j_1, j_2) F_{j, j_1, j_2, J}(\omega_1, \omega_2) Y_{L, 0}(\beta, 0) Y_{J, M}(\hat{k}_e)$$

where the first photon polarisation μ_1 (spherical component) is direct along the laboratory z -axis, the second photon polarisation μ_2 lies in the x, z planes making an angle β with the z -axis and \hat{k}_e is the unit vector which specifies the photoelectron direction. The A coefficients are geometrical factors while the molecular properties are all embodied in the F coefficients which are the quadratic forms of (in general) all possible transition amplitudes, computed in the fixed body frame,

$$\begin{aligned} & m_{\{\lambda_M\} \leftarrow \{\lambda_M\}}^{(2)}(\omega_1, \mu_1, \omega_2, \mu_2) \\ &= (1 + \mathcal{P}_{1,2}) \sum_M \frac{\langle \Phi_{\{\lambda_0\}} \hat{O}_{\mu_1} \Phi_{\{\lambda_M\}} \rangle \langle \Phi_{\{\lambda_M\}} \hat{O}_{\mu_2} \Phi_{j,\varepsilon,l,m}^{(-)} \rangle}{\omega_2 - E_M + E_0} \\ &= (1 + \mathcal{P}_{1,2}) \langle \Phi_{\{\lambda_0\}} \hat{O}_{\mu_1} \hat{G}_{elec}^+(\omega_2 + E_{0,v_0}) \hat{O}_{\mu_2} \Phi_{j,\varepsilon,l,m}^{(-)} \rangle \mathbf{Q}_0, \end{aligned} \quad (1)$$

where the final state $|\Phi_{j,\varepsilon,l,m}^{(-)}\rangle$ in the continuum is labelled by the partial wave (l, m) channel (j, ε) indices. The available methods to compute $M^{(2)}$ resort generally either to estimate the summation-integration (upon the continuum) by a sum upon a finite set of approximate states or to the response functions which through their poles and residues supply the excitation energies and the transition density matrices. The first approach requires the determination of quite a number of excited states in order to have a satisfactory approximation of the sum. Furthermore the states should be accurate enough to yield reliable values of the transition matrix elements which, as is well known, are very sensitive quantities. For example table 1 reports some results which show:

(i) that the Hartree–Fock HF approximation may give results very inaccurate (mainly between excited states) if compared with the much more accurate results yielded by more sophisticated calculations.

(ii) the ambiguity which arises from the differences in the results obtained by employing different gauges.

Figure 1 reports some results for one-photon photoabsorption cross-section calculations for HCl made with increasingly accurate (MC–SEA–FOA \rightarrow SC–RPA \rightarrow

Table 1. Transition matrix elements results. HF and CI calculated values. Length gauge/velocity gauge.

Helium	HF ^a	CI ^b	
1s ² 1S–1s2p ¹ P	0.187/0.262	0.2754/0.2753	
1s2s 1S–1s3p ¹ P	0.248/0.666	0.1512/0.1512	
Beryllium	HF	CI ^c	Hylleraas ^d
2S ² 1S–2s2p ¹ P	1.777/1.013 ^e	1.385/1.331	1.3436
2s2p ¹ P–2p ² 1D	0.164/2.060 ^f	0.0006/0.0002	
2s2p ³ P–2p ² 3P	0.546/0.354 ^f	0.449/0.412	
Magnesium	HF ^g	CI ^g	CI ^h
3s ² 1S–3s3p ¹ P	1.783/0.913	1.746/1.676	1.761/1.746
3s3p ¹ P–3s4s 1S	0.206/0.033	0.174/0.124	0.155/0.153
Ionized aluminium	HF ^g	CI ^g	
3s3p ¹ P–3p ² 1D	0.658/2.618	0.002/0.001	

^a Roginsky *et al* 1983; ^b Cacelli *et al* 1982; ^c Moccia and Spizzo 1985;

^d Sims and Whitten 1973; ^e Burke *et al* 1971; ^f Hibbert 1974; ^g Weiss 1967; ^h Moccia and Spizzo 1988.

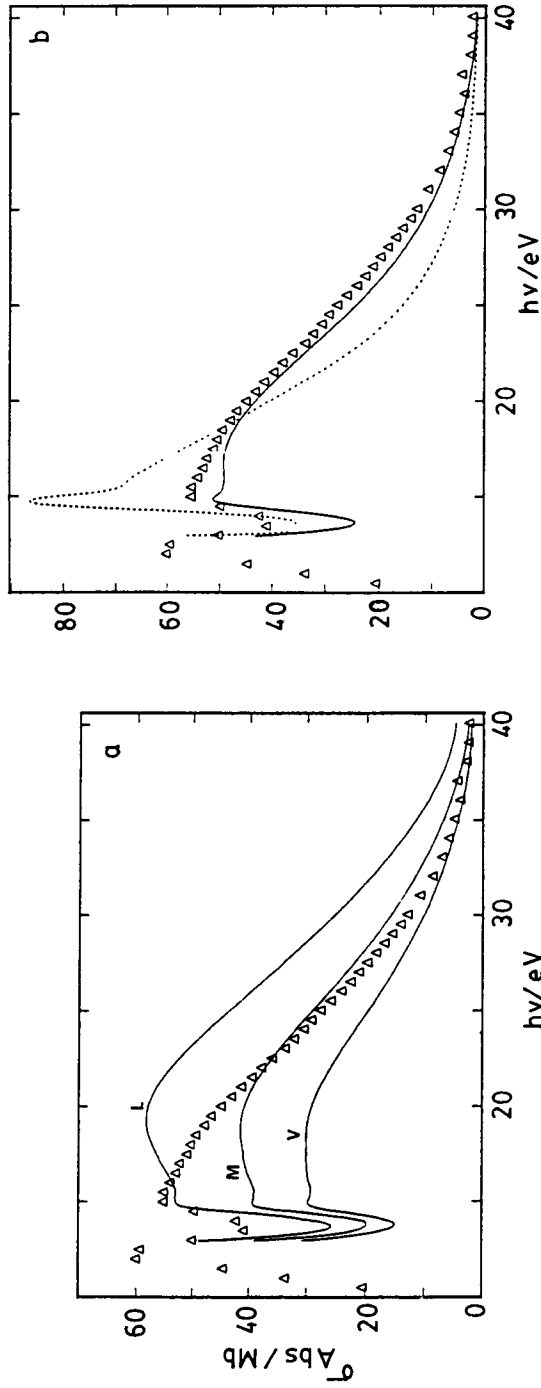


Figure 1. (a) Photoabsorption cross-section of HCl by MC-SEA-FOA calculation in length L , velocity V and mixed M gauge with experimental energy loss data (David *et al* 1984) versus photon energy. (b) The same by MC-RPA (full line) and SC-RPA (broken line).

MC-RPA) theoretical approaches (Cacelli *et al* 1986). For the last two methods the agreement between the length- and the velocity-gauge results is satisfactory which (at least formally) eliminates the choice of the gauge ambiguity.

2. Calculation of states

The need to have accurate electronic states may be achieved by several means but nowadays the most reliable one is doubtless the configuration interaction (CI) approach or one of its many reduced versions (see for instance Wilson 1987). This approach, however, by increasing the orbital basis size, rapidly reaches unmanageable dimensions. For instance if m is the number of orbitals and the system is characterized by n_α spin $+1/2$ and n_β spin $-1/2$ the number of the configuration function states (CES) (neglecting the spatial symmetry which may reduce somewhat the number) is $[m!/n_\alpha!(m-n_\alpha)!][m!/n_\beta!(m-n_\beta)!]$ which, in the case of 1A_1 states of NH_3 with $m = 35$ (double ζ basis plus 1 polarization type function for nucleus, a rather modest basis!) is $\approx 10^9!$

Quite noticeable efforts have been dedicated to make these CE calculations possible and nowadays different algorithms and codes are available (Knowles and Handy 1989, and references therein) which may implement calculations of this size.

Notwithstanding the great ingenuity which characterizes all these algorithms the need to have less brute force techniques is evident and several approaches which try to focus all efforts upon the most important configurations have been proposed and implemented with success (Wilson 1987). Unfortunately they, as the more straightforward CI, suffer from the unavoidable lack of capability of yielding accurate description of the higher excited states particularly the states in the continuum. In fact the states which are characterized by being much more diffuse than the ground and first states would require a very large increase of the basis with the inclusion of special functions which do not have the nice analytical properties of the GTO's. The problem is simplified when there are sufficient justifications to limit the CI to a reduced number of "active" electrons. In such a case it is possible (also through the use of effective potentials of the "core" which may take semiempirically into account the core-active shell correlation) to attain a good accuracy with a very reduced number of CFS's.

3. The response functions method

A different approach is based upon the methods which attempt to compute directly the response functions of the system. When a system is subjected to a time-dependent perturbation $\hat{h}(t) = \lambda_a V(t) + \lambda_b W_b(t)$ the Fourier transform of the linear response $\langle\langle A; V_a \rangle\rangle_t$

$$R^{(1)}(\omega_1) = \sum_{\mu} \left\{ \frac{A_{0,\mu} V_{\mu,0}(\omega_1)}{\omega_1 - \omega_{\mu} + i0^+} - \frac{A_{0,\mu} V_{\mu,0}(\omega_1)}{\omega_1 + \omega_{\mu} + i0^+} \right\}, \quad (2)$$

(with $A_{\mu,\nu} = \langle \Phi_{(\lambda_a)} | \hat{A} | \Phi_{(\lambda_b)} \rangle$ etc.) shows that its residues and poles correspond to the ground-excited states transition matrix elements and to the excitation energies. The

(two-times) Fourier transform of the quadratic response $\langle\langle A; V; W \rangle\rangle_t$

$$\begin{aligned}
 R^{(2)}(\omega_1, \omega_2) = \sum_{\mu}^{\prime} \sum_{\nu}^{\prime} \left\{ \frac{A_{0,\mu} V_{\mu,\nu}(\omega_1) W_{\nu,0}(\omega_2)}{(\omega_1 + \omega_2 - \omega_{\mu} + i0^+)(\omega_2 - \omega_{\nu} + i0^+)} \right. \\
 + \frac{W_{0,\mu}(\omega_2) V_{\mu,\nu}(\omega_1) A_{\nu,0}}{(\omega_1 + \omega_2 + \omega_{\nu} + i0^+)(\omega_2 + \omega_{\mu} + i0^+)} \\
 + \frac{A_{0,\mu} W_{\mu,\nu}(\omega_2) V_{\nu,0}(\omega_1)}{(\omega_1 + \omega_2 - \omega_{\mu} + i0^+)(\omega_1 - \omega_{\nu} + i0^+)} \\
 + \frac{V_{0,\mu}(\omega_1) W_{\mu,\nu}(\omega_2) A_{\nu,0}}{(\omega_1 + \omega_2 + \omega_{\nu} + i0^+)(\omega_1 + \omega_{\mu} + i0^+)} \\
 - \frac{W_{0,\mu}(\omega_2) A_{\mu,\nu} V_{\nu,0}(\omega_1)}{(\omega_2 + \omega_{\mu} + i0^+)(\omega_1 - \omega_{\nu} + i0^+)} \\
 \left. - \frac{V_{0,\mu}(\omega_1) A_{\mu,\nu} W_{\nu,0}(\omega_2)}{(\omega_1 + \omega_{\mu} + i0^+)(\omega_2 - \omega_{\nu} + i0^+)} \right\}, \quad (3)
 \end{aligned}$$

shows that its residue at $\omega_2 = \omega_{\lambda}$ (with $\omega_1 \rightarrow -\omega_1$) is

$$\sum_{\mu}^{\prime} \left\{ \frac{A_{0,\mu} V_{\mu,\nu} W_{\nu,0}}{(-\omega_1 + \omega_{\lambda} - \omega_{\mu} + i0^+)} - \frac{V_{0,\mu} A_{\mu,\nu} W_{\nu,0}}{(-\omega_1 + \omega_{\mu} + i0^+)} \right\} W_{\lambda,0},$$

which for $\omega_1 + \omega_2 = \omega_{\lambda}$ gives

$$\left\{ \sum_{\mu}^{\prime} \left[\frac{A_{0,\mu} V_{\mu,\nu} W_{\nu,0}}{(\omega_2 - \omega_{\mu} + i0^+)} - \frac{V_{0,\mu} A_{\mu,\nu} W_{\nu,0}}{(\omega_1 - \omega_{\mu} + i0^+)} \right] \right\} W_{\lambda,0}.$$

The last quantity in brackets is the required two-photon transition amplitude (1). Exploiting either a variational principle for time-dependent Hamiltonians (Moccia 1974; McWeeny 1983) or the Erhenfest theorem applied to some adequately defined excitation operators $\hat{O}_{\{\lambda_{\mu}\}}^{\dagger}$ (Olsen and Jorgensen 1985) it is possible to obtain approximations of the response functions. These methods yield the following form for the linear response

$$R^{(1)}(\omega_1) \simeq \sum_I \left\{ \frac{\bar{A}_{0,I} \bar{V}_{I,0}(\omega_1)}{\omega_1 - \bar{\omega}_I + i0^+} - \frac{\bar{V}_{0,I}(\omega_1) \bar{A}_{I,0}}{\omega_1 + \bar{\omega}_I + i0^+} \right\}$$

which has the same structure of the correct expression (2). Thus it is justified to consider the $\bar{A}_{0,I}$ and $\bar{V}_{I,0}$ as the transition matrix elements and the $\bar{\omega}_I$ as the excitation energies.

More difficult is the interpretation of the resulting expression of the quadratic response function

$$\begin{aligned}
 R^{(2)}(\omega_1, \omega_2) \simeq \sum_I \sum_n \left\{ \frac{a_{0,I} v_{I,n}(\omega_1) w_{n,0}(\omega_2)}{(\omega_1 + \omega_2 + \bar{\omega}_I + i0^+)(\omega_2 + \bar{\omega}_n + i0^+)} + \dots \right. \\
 \left. \text{all possible denominators} \right\} +
 \end{aligned}$$

$$+ \sum_j \sum_l \sum_n \left\{ \frac{q_{0,j} w_{j,l}(\omega_2) a_{l,n} v_{n,0}(\omega_1)}{(\omega_1 + \omega_2 - \bar{\omega}_j + i0^+)(\omega_2 - \bar{\omega}_l + i0^+)(\omega_1 - \bar{\omega}_n + i0^+)} + \dots \right\},$$

which exhibits several terms absent in the correct expression (3). It is possible however, by making additional approximations, to obtain a simplified expression for the two-photon transition amplitude (1) with the same structure as the correct one.

First of all it may be observed that the linear response already provides approximations for the ground-state excited states transition matrix elements and of the corresponding excitation energies. On the other hand it may be shown that the excited states transition matrix elements may be expressed as (Yeager and Jørgenson 1979; Oddershede *et al* 1984)

$$\langle \Phi_{\{i_M\}} | \hat{O}_{\mu_2} | \Phi_{\{i_M\}} \rangle \simeq \langle \Phi_{\{i_0\}} | [\hat{O}_{\{i_M\}}, \hat{O}_{\mu_2}, \hat{O}_{\{i_M\}}] | \Phi_{\{i_M\}} \rangle + \frac{1}{2} \langle \Phi_{\{i_0\}} | [[\hat{O}_{\{i_M\}}, \hat{O}_{\{i_M\}}]_-, \hat{O}_{\mu_2}]_+ | \Phi_{\{i_0\}} \rangle, \quad (4)$$

where

$$[A, B, C] = \frac{1}{2} \{ [A, [B, C]] + [[A, B], C] \}.$$

If random phase approximation (RPA) may be considered a sufficient approximation i.e.

$$| \Phi_{\{i_0\}} \rangle = | \Phi_0 \rangle_{\text{SCF}}; \quad \hat{O}_{\{i_M\}}^\dagger = \sum_{rs} (X_{rs, \{i_M\}} \hat{a}_r^\dagger \hat{a}_s + Y_{rs, \{i_M\}} \hat{a}_s^\dagger \hat{a}_r),$$

then (for the more general case of non-orthogonal virtual orbitals) (Cacelli *et al* 1989)

$$\begin{aligned} \langle \Phi_{\{i_M\}} | \hat{O}_\mu | \Phi_{\{i_M\}} \rangle &\simeq \sum_{i, v, v'} \{ X_{vi, M}^* X_{v'i, M'} \langle v | \hat{O}_\mu | v' \rangle + Y_{vi, M}^* Y_{v'i, M'} \langle v' | \hat{O}_\mu | v \rangle \} - \\ &- \sum_{i, i', v, v'} \{ X_{vi, M}^* X_{v'i', M'} \langle i' | \hat{O}_\mu | i \rangle \langle v | v' \rangle + Y_{vi, M}^* Y_{v'i', M'} + \\ &+ \langle i | \hat{O}_\mu | i' \rangle \langle v' | v \rangle \} + \delta_{M, M'} \langle \Phi_{\{i_0\}} | \hat{O}_\mu | \Phi_{\{i_0\}} \rangle. \end{aligned} \quad (5)$$

This last expression, or the more accurate one (5), provides the required matrix elements which, together with the quantities already supplied by the RPA, allow the evaluation of (1). The expressions (5) are further simplified if the final state is approximated as $| \Phi_{j, \varepsilon, l, m} \rangle \simeq \hat{a}_{j, \varepsilon, l, m}^\dagger \hat{a}_j | \Phi_{\{i_0\}} \rangle$. Thus (Cacelli *et al* 1989)

$$\begin{aligned} \langle \Phi_{\{i_M\}} | \hat{O}_\mu | \Phi_{j, \varepsilon, l, m} \rangle &\simeq \sum_v X_{vj, M}^* \{ \langle v | \hat{O}_\mu | j, \varepsilon, l, m \rangle + \langle v | j, \varepsilon, l, m \rangle \langle \Phi_{\{i_0\}} | \hat{O}_\mu | \Phi_{\{i_0\}} \rangle \} \\ &- \sum_{i, v} X_{vi, M}^* \langle v | j, \varepsilon, l, m \rangle \langle j | \hat{O}_\mu | i \rangle. \end{aligned} \quad (6)$$

4. States in the continuum

Most of the several quantum chemical *ab initio* methods presently available have been applied to the calculation of bound molecular states. They are generally based on the projection of the Schrodinger equation on a finite set of square integrable

(L^2) functions. The unquestionable success of such techniques has recently drawn the attention of theoreticians who generally describe the electronic continuum by “scattering” techniques which present several difficulties also because of the multi-center nature of the problem in molecules. Methods based on the description of the molecular electronic continuum by L^2 functions have some definitive advantage over the traditional scattering methods. In fact the algorithm may be reduced to a sequence of matrix operations that can be efficiently implemented on modern supercomputers. Moreover the L^2 methods can easily allow different levels of approximation in the calculations which, on the other hand, may be carried out by the well-established computer codes already developed to treat bound-state problems. Even at the lowest approximation level, realistic multi-center non-local potentials like the Hartree–Fock potential can be easily handled for the description of the electron-molecule (ion) interaction.

A very convenient method based upon the energy variational approach, originally pioneered by Fano (1961) may be adapted to the usual L^2 basis set approach of quantum chemistry.

The method (Cacelli *et al* 1986; Moccia and Spizzo 1990a) is essentially a CI carried out with a basis set formally including the continuum. By a judicious choice of the “unperturbed” basis states the resulting secular equation is solved, at a given energy E lying in the continuum, by the reaction \mathbf{K} -matrix technique which yields an integral equation in the space of the half-off-shell \mathbf{K} -matrix expansion coefficients. These integral equations are solved by introducing a discrete quadrature upon the grid points supplied by a discretized description of the “unperturbed” states which turns the integral equations into a set of linear equations. The matrix elements at arbitrary values of the continuous indices are interpolated upon the grid points.

This method affords the calculation of the properties pertaining to the continuum either at the single orbital approximation (Cacelli *et al* 1986, 1989) or at a more sophisticated CI-type level (Moccia and Spizzo 1990a,b). The accuracy attained by this L^2 method with a careful choice of particular basis functions, is exemplified by the results (Moccia and Spizzo 1990a, b) shown in figure 2.

5. Numerical results

Figure 3 reports the results for the two-photon ionisation cross-section of Mg (Moccia and Spizzo 1988, 1989). The calculations were carried out using a CI limited, to the two-electron valence shell while the interaction with the core was that yielded by the static-exchange approximation (SEA) plus a polarization term which accounts for the intershell correlation. The states lying in the continuum were obtained by the L^2 \mathbf{K} -matrix methods outlined in the previous section. This approach yields results, which include quite a number of observables (term energies, positions and widths of the resonances, transition probabilities, states lifetime etc. for the $1,3S^e$, $1,3P^o$, $1,3D^e$, $1,3P^e$ manifolds) in excellent agreement with the available experimental data. Unfortunately, for the time being, there are not quantitative experimental results to be compared with the calculations shown in figure 3. A partial comparison may be made with the one colour experiment (Bonanno *et al* 1986) made in the restricted range 290–295 nm (see figure 4). It should be noticed that this energy range is particularly interesting since it involves an intermediate state resonance and a final autoionising state (the

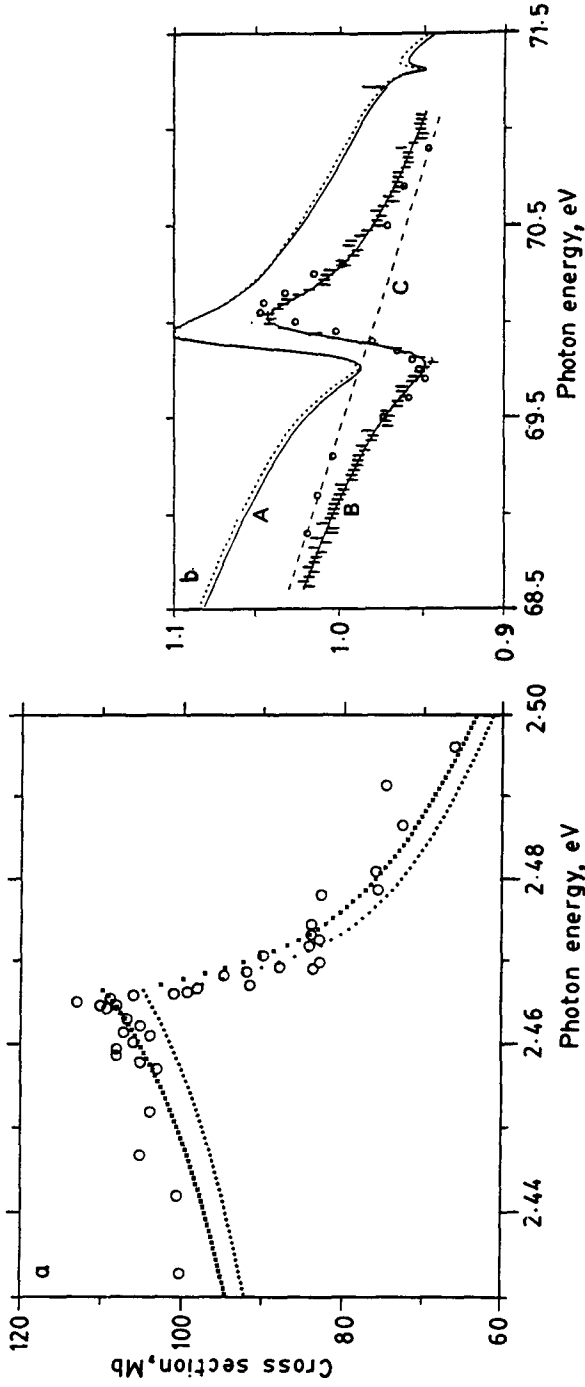


Figure 2. (a) Photodetachment cross-section at the $2p$ threshold of Li^- . +: LG results, \times : VG results, \circ : experiment (Bae and Petersen 1985). (b) Detail of the total cross-section around the 1_3 autoionising resonance of He. A: Calculated values, LG (full line) and VG (broken line) results. B: experimental results of Kossman *et al* (1988) (error bars) and their interpolation without (solid line) and with (dotted line) correction for the monocromator band pass. C: experimental results of Kossman *et al* (1988) for the assumed background. \circ : experimental results of Lindle *et al* (1987).

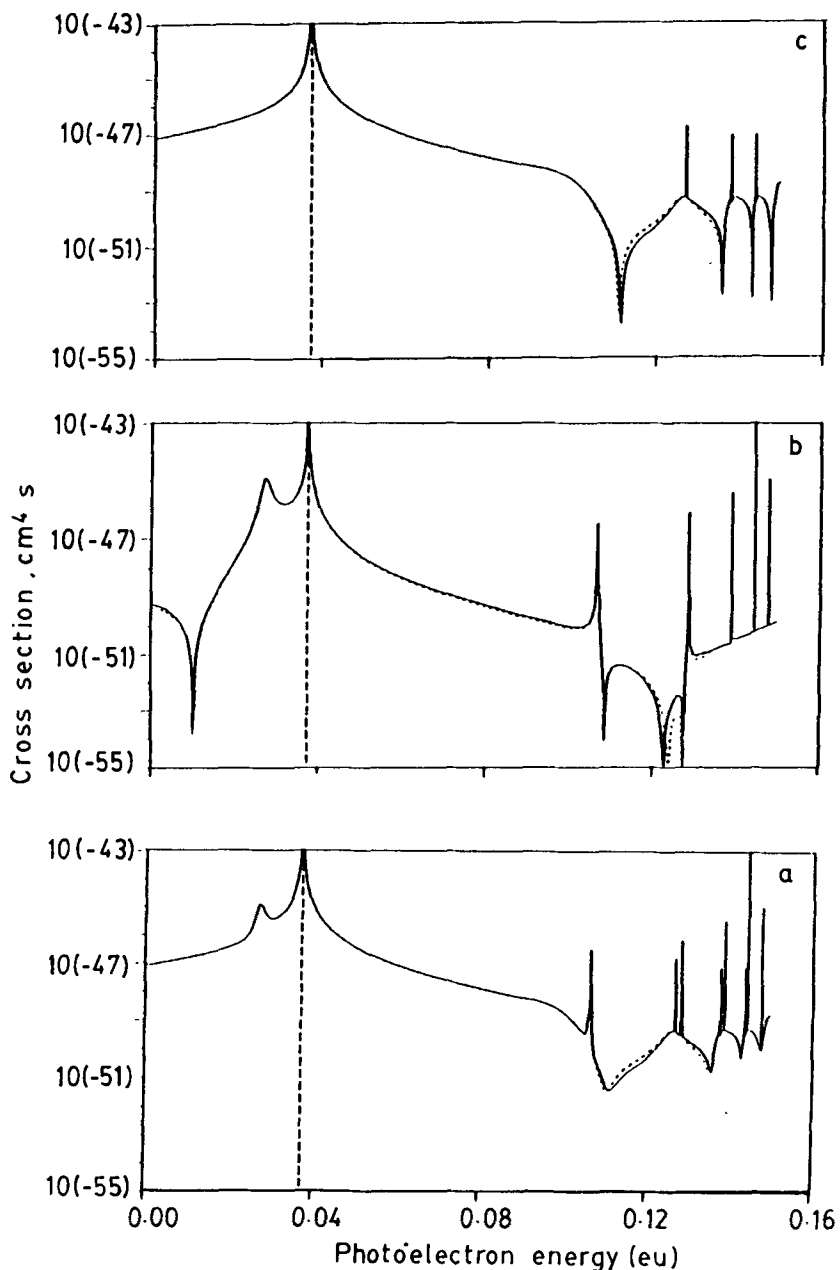


Figure 3. Two-photon ionisation cross-section from ground state of Mg. (a) Total ionisation cross-section. Full line LG results; broken line VG results. The vertical broken line indicates the position of the intermediate state resonance due to the $3s3p\ ^1P^o$ state. (b) the S -wave contribution. (c) The D -wave contribution.

$3s^2$ of the $^1S^e$ manifold) which represents a rather severe test for the theory. The satisfactory agreement shows also that the LOPT in this case is valid even for energies quite close to the intermediate resonance.

Figures 5 and 6 report the results of the two-photon ionisation cross-section of

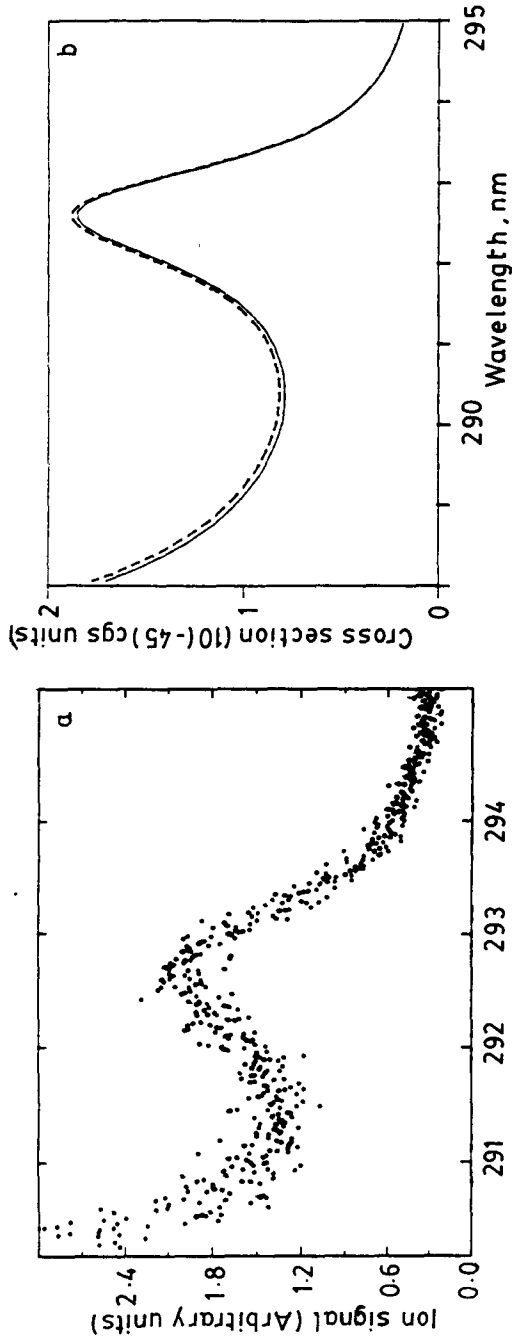


Figure 4. (a) Experimental results (Bonanno *et al* 1986) of the total two-photon ionisation cross-section from the ground state of Mg. Single beam experiment; linear polarization. (b) Theoretical results; full line LG; broken line VG.

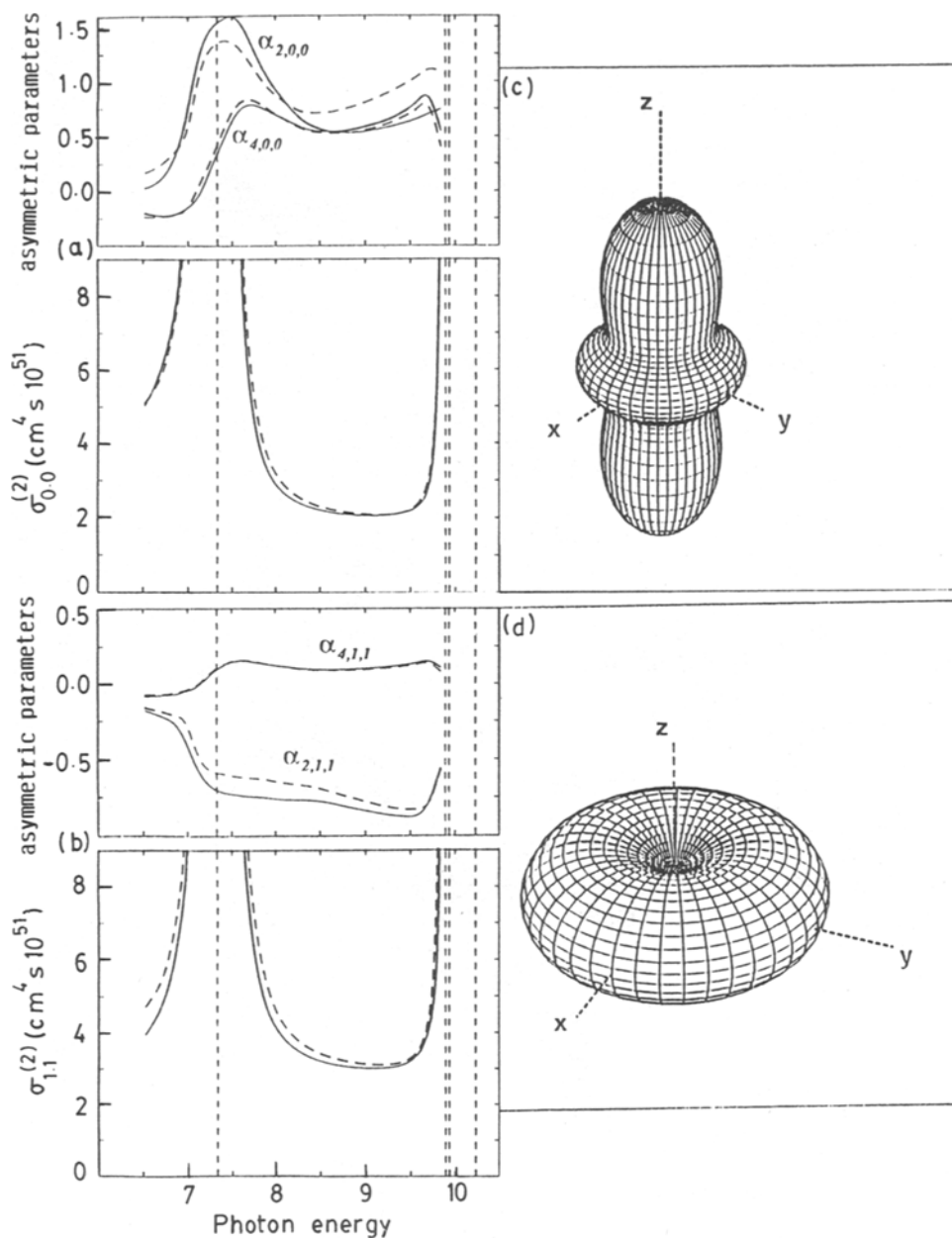


Figure 5. (a) Integral cross section $\sigma_{0,0}^{(2)}$ and asymmetry parameters $\alpha_{2,0,0}$, $\alpha_{4,0,0}$ (see Cacelli *et al* 1990) for a two-photon ionisation process in H_2O . Single beam, linear polarisation. Full line LG, broken line VG. Vertical lines indicate the position of intermediate state resonances. (b) Analogous results for the asymmetry parameters $\alpha_{2,1,1}$, $\alpha_{4,1,1}$ (see Cacelli *et al* 1990); single beam circularly polarized photons. (c) Photoelectron angular distribution for a two-photon ionisation process in H_2O . Single beam, linearly polarized photons which an energy of 9.02 eV. VG results. (d) Analogous results of photoelectron angular distribution. Single beam, circularly polarized photons. VG results.

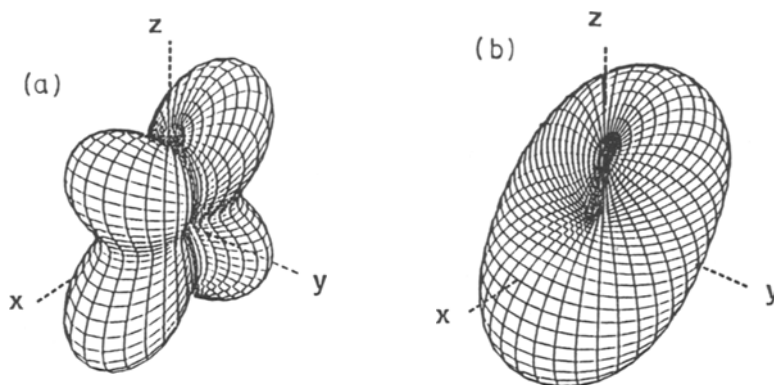


Figure 6. (a) Photoelectron angular distribution for a two-photon ionisation process in H_2O . Two linearly polarized photon with energy of 9.02 eV at an angle $\beta = 90^\circ$ between the polarisation directions. (b) Same as (a) for two circularly polarized photons.

H_2O (Cacelli *et al* 1990) obtained using the RPA to compute the ground-excited states matrix elements and the excitation energies, while the relation (6) was exploited to calculate the excited-excited states transition matrix elements. The final orbitals lying in the continuum, used in (6), were determined by the L^2 K-matrix methods applied to the one-electron hamiltonian at the SEA level. Since the results were obtained in the VTA they may be trusted for photon energies sufficiently far from the rotovibrational envelope corresponding to intermediate electronic excitations. With some caution the calculated values in the energy interval from 8.2 to 9.4 eV may be considered to give a satisfactory representation of the situation. More interesting is the dependence of the angular distribution of the photoelectrons upon the experimental set-up. This distribution is reported in figures 5 and 6 for a variety of experimental settings at the photon energy of 9.02 eV where the calculated values may be considered reliable. Since the orientational average depends in a complicated way upon all the possible transition amplitudes it is not easy to figure out in simple terms the final angular distribution. Finally it should be noted that when one of the two photons is circularly polarized the angular distribution will display a slight asymmetry with respect to the plane defined by the two polarization of the photons due to the asymmetry induced by the photon field.

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