Electron and ion angular distributions in resonant
dissociative photoionization of H$_2$ and D$_2$ using
linearly polarized light

Jorge Fernández and Fernando Martín
Departamento de Química C-9, Universidad Autónoma de Madrid,
28049 Madrid, Spain
E-mail: fernando.martin@uam.es

New Journal of Physics 11 (2009) 043020 (34pp)
Received 7 January 2009
Published 15 April 2009
Online at http://www.njp.org/
doi:10.1088/1367-2630/11/4/043020

Abstract. We have evaluated fully differential electron angular distributions in
H$_2$ and D$_2$ dissociative photoionization by using linearly polarized light of 20, 27
and 33 eV. At 20 eV, the distributions exhibit simple p-wave patterns, which is the
signature of direct ionization through the X$^2\Sigma_g^+$ (1s$\sigma_g$) channel. At 27 eV, where
the Q$_1$ autoionizing states are populated, we observe a similar pattern, except
when the molecule is oriented perpendicularly to the polarization direction and
the energy of the ejected electron is small. In contrast, at 33 eV, autoionization
from the Q$_1$ and Q$_2$ states leads to interferences between the X$^2\Sigma_g^+$ (1s$\sigma_g$) and
2$^2\Sigma_u^+$ (2p$\sigma_u$) ionization channels that result in a strong asymmetry of the electron
angular distributions along the molecular axis. This asymmetry changes rapidly
with the energy of the ejected electron. Electron angular distributions integrated
over all possible molecular orientations or ion angular distributions integrated
over electron emission angle show no reminiscence of the above phenomena,
but the corresponding asymmetry parameters dramatically change with electron
and ion energies in the region of autoionizing states.
1. Introduction

Angle-resolved photoelectron spectroscopy has been used for more than 70 years to investigate the photoionization dynamics of atoms and molecules. Since its first application to atoms in the 1930s [1] until the sophisticated coincidence experiments performed in more recent times, a vast number of photoionization problems have been investigated. In particular, in the last few years, complete molecular photoionization experiments, in which the momentum of all the ejected electrons and atomic ions is determined in coincidence, have become available [2]–[9]. This technique, usually called ‘cold target recoil ion momentum spectroscopy’ (COLTRIMS), has given access to fully differential photoelectron angular distributions associated with well-defined orientations of the molecule with respect to the polarization direction and energies of the ejected electrons or atomic ions.

A significant experimental effort has been devoted to obtaining fully differential photoelectron angular distributions in the simple H₂ and D₂ molecules [4, 7], [10]–[15]. These experiments have already led to the discovery of interesting phenomena that were hidden in the earlier experiments in which only the proton or deuteron kinetic energy release (KER) could be determined (see e.g. [16, 17]). In the case of single ionization, a striking finding is the observation of asymmetric photoelectron angular distributions that reflects the breaking of molecular symmetry [7], i.e. emission of a photoelectron with subsequent dissociation of the remaining H⁺ fragment shows no symmetry with respect to the ionic H⁺ and neutral H atomic fragments. In [7], asymmetry was observed by using linearly polarized light of 33 eV and for D₂ molecules oriented perpendicular to the polarization direction. The origin of the asymmetry was attributed to the presence of autoionising states. A similar finding was reported earlier in [4], where some evidence of asymmetry in molecules oriented parallel to the polarization direction was also provided.

In spite of the apparent simplicity of the H₂ and D₂ molecules, the calculation of fully differential angular distributions in the photon energy region where resonant states are
accessible is a formidable task. Autoionization is the result of electron correlation and any theoretical attempt to describe the above observations must thus account for it. Furthermore, H₂ autoionizing states are dissociative and, since these states lose one of their electrons after a few femtoseconds, the nuclei have enough time to move outside the Franck–Condon (FC) region before the electron is effectively ejected. Hence the need to account for the nuclear motion as well. Finally, since direct ionization and autoionization interfere, a fully quantum mechanical treatment of both the electronic and nuclear motions is required. A theoretical framework that fulfils all the above requirements has been proposed in [18, 19] (see also [20] for a review). It has been successfully applied to study a variety of different ionization problems in H₂, such as resonant dissociative photoionization [18]–[23], resonant electron impact ionization [24] and resonant ion impact ionization [25]. In [7], this method had to be extended to account for the special boundary conditions associated with COLTRIMS experiments.

Apart from [7], all previous theoretical works on H₂ or D₂ autoionizing states have exclusively provided proton and deuteron kinetic energy distributions integrated over electron emission angle [18]–[25]. Calculations of electron angular distributions resulting from single ionization of H₂ are scarce and have either considered photon energy regions where doubly excited states are barely populated, e.g. at very high photon energy [26]–[28], or neglected the nuclear motion [29], which is not appropriate when doubly excited states are significantly populated. In this paper, we present photoelectron angular distributions that arise in resonant dissociative photoionization of H₂ by using an extension of the theoretical method described in [20], which incorporates electron correlation and nuclear motion and is therefore suitable to describe H₂ autoionization. In the next section, we will explain the details of the theoretical method used in [7] with emphasis on the extensions that are required to properly account for the boundary conditions of a COLTRIMS experiment. This is necessary to provide photoelectron angular distributions that are directly comparable with those obtained in such experiments. To obtain a deeper insight on the role of autoionizing states in inducing asymmetric photoelectron angular distributions, we study dissociative photoionization not only of H₂ but also of D₂ and consider other photon energies and molecular orientations than those reported in [7]. In particular, we have chosen photon energies of 20, 27 and 33 eV, for which one expects that autoionization will play no role (20 eV) or will involve the Q₁ (27 eV) or Q₂ (33 eV) doubly excited states of H₂. Three typical orientations of the molecule have been selected: 0° (parallel to the polarization direction), 54.7° (the ‘magic’ angle) and 90° (perpendicular). The reason for choosing an orientation different from parallel and perpendicular is that, in contrast to the latter, ionization proceeds through a coherent superposition of ¹Σ⁺ u and ¹Π a states and not through a pure molecular symmetry. The magic angle is chosen in most experiments (see e.g. [4] and references therein) because, for this particular orientation, the shape of the proton kinetic energy distribution coincides with that produced by a set of randomly oriented molecules. Since, for randomly oriented molecules, photoelectron angular distributions are much easier to measure, we also report calculations for the electronic asymmetry (beta) parameter that fully determines these distributions. We also present results for the ionic asymmetry (beta) parameter, which is useful to predict the angular distribution of the ionic fragments H⁺ or H⁺⁺ irrespective of the electron emission angle. For a better understanding of the physical origin of the angular distributions reported in this work, we also include the proton and deuteron kinetic energy spectra.
that result from integration of the former distribution with respect to the electron emission angle. These spectra will be compared with those previously calculated at 27 and 33 eV [18, 19, 21].

Atomic units \((m_e = \hbar = e = 1)\) are used throughout unless otherwise stated.

2. General formalism

Photoionization cross sections have been evaluated in the framework of the dipole approximation. The fully differential photoionization cross section, also called the molecular frame photoelectron angular distribution (MFPAD), is differential in both the energy and direction of the ejected electron, the energy and orientation of the ejected \(H^+\) (or \(H^2^+\) molecular ion) and the orientation of the polarization vector with respect to the molecular axis. It is given by \([30]\)

\[
\frac{d\sigma^{\mu_0}(\omega)}{d\Omega_d d\Omega_e d\varepsilon_a} = \frac{4\pi^2 \omega}{c} \sum_{\mu_a, \mu_b} \sum_{\ell_a, m_a} \sum_{\ell_b, m_b} i^{(\ell_a - \ell_b)} e^{i(\hat{\sigma}_{\ell_a} - \hat{\sigma}_{\ell_b})} (-1)^{m_a + \mu_a - \mu_0} T^{e}_{\alpha \ell_a m_a \mu_a}(\varepsilon_a) \\
\times T_{\alpha \ell_b m_b}(\varepsilon_a) \sum_{L_c} \left[ \frac{(2\ell_a + 1)(2\ell_b + 1)}{(2L_c + 1)} \right]^{1/2} C(\ell_a, \ell_b, L_c; -m_a, m_b, M_c) \\
\times C(\ell_a, \ell_b, L_c; 0, 0, 0) Y^{M_c*}_{L_c}(\theta_e, \phi_e) \sum_{L_f} \left[ \frac{1}{(2L_f + 1)} \right]^{1/2} \\
\times C(1, 1, L_f; -\mu_a, \mu_b, M_f) C(1, 1, L_f; -\mu_0, \mu_0, 0) Y^{M_f}_{L_f}(\theta_p, \phi_p) \tag{1}
\]

with

\[
\mu_a, b = 0, \pm 1, \quad M_f = -\mu_a + \mu_b, \quad M_c = -m_a + m_b, \\
\ell_a + \ell_b \geq L_c \geq |\ell_a - \ell_b| \quad \text{and} \quad 2 \geq L_f \geq 0.
\]

In this equation, \(\mu_0 = 0\) for linearly polarized light and \(\mu_0 = \pm 1\) for circularly polarized light, \(\alpha\) denotes the electronic state of the residual molecular ion, \(\hbar \omega\) is the photon energy, \(c\) is the speed of light, \(\varepsilon_a\) is the photoelectron energy in channel \(\alpha\), \(\Omega_e = (\theta_e, \phi_e)\) is the photoelectron emission direction in the molecular frame (\(\theta_e\) and \(\phi_e\) are the polar angles), \(\Omega_a = (\theta_h, \phi_h)\) is the polarization direction with respect to the molecular axis \(z\), \(C(j_1, j_2; j; m_1, m_2, m)\) denotes a Clebsch–Gordan (CG) coefficient, \(Y^M_L(\theta, \phi)\) is a spherical harmonic, \(\hat{\sigma}_\ell(\varepsilon_a) = \arg(\ell + 1 - i/\sqrt{2\varepsilon_a})\) is the Coulomb phase shift and \(T_{\alpha \ell_a m_a \mu}(\varepsilon_a)\) is the transition dipole matrix element given by

\[
T_{\alpha \ell_a m_a \mu}(\varepsilon_a) = \int dR \langle \Psi^-_{\alpha \nu_a \ell_a m_a \varepsilon_a}(\mathbf{r}, \mathbf{R}) | e_\mu \cdot \mathbf{D} | \Psi^-_{\nu_v \ell_v m_v \varepsilon_v}(\mathbf{r}, \mathbf{R}) \rangle, \tag{2}
\]

where \(\Psi^-_{\nu_v}\) is the ground molecular state of energy \(W^-_{\nu_v}\), \(\Psi^-_{\alpha \nu_a \ell_a m_a \varepsilon_a}\) is the final molecular state of energy \(W^-_{\nu_a} + \varepsilon_a\) representing a molecular ion in the \(\nu_a\) vibronic state (either dissociative or nondissociative) and an ionized electron of energy \(\varepsilon_a\) and angular momentum \(\ell_a m_a\), \(\mathbf{r}\) represents the electronic coordinates, \(\mathbf{R}\) is the internuclear distance, \(e_\mu\) is the photon polarization vector,
and $\mathbf{D}$ is either $\sum_i r_i$ (length gauge) or $(\hbar \omega)^{-1} \sum_i \nabla_i$ (velocity gauge). Energy conservation implies that
\[
W_{gy} + \hbar \omega = W_{\nu_a} + \varepsilon_a.
\] (3)

We note that, for the sake of simplicity, the label $\alpha$ is not explicitly written in the $\ell_a$, $\ell_b$, $m_a$ and $m_b$ indexes used in the summations, although for each $\alpha$ there is a summation involving such indexes.

As shown in [31], for linearly polarized light, equation (1) is formally equivalent to writing
\[
\frac{d\sigma_{\mu_a=0}(\omega)}{d\Omega_a d\Omega_e d\varepsilon_a} = F_{00}^0(\omega, \varepsilon_a, \theta_e) + F_{00}^0(\omega, \varepsilon_a, \theta_e) P_2^0(\cos \theta_n) + F_{21}^0(\omega, \varepsilon_a, \theta_e) \times P_1(\cos \theta_n) \cos(\phi_e - \phi_n) + F_{22}^0(\omega, \varepsilon_a, \theta_e) P_2(\cos \theta_n) \cos(2[\phi_e - \phi_n]),
\] (4)

where the $F_{\mu \nu}^{\mu \nu}(\omega, \varepsilon_a, \theta_e)$ functions are written as an expansion in terms of Legendre polynomials
\[
F_{\mu \nu}^{\mu \nu}(\omega, \varepsilon_a, \theta_e) = \sum_{L'} C_{L' L N}^{\mu \nu}(\omega, \varepsilon_a) P_{L'}(\cos \theta_e),
\] (5)

with
\[
C_{L' L N}^{\mu \nu}(\omega, \varepsilon_a) = \frac{2 \pi \omega}{c} (-1)^N (-i)^{\delta_{L',0}} \sum_{\mu_a, m_b^+} \sum_{\mu_b, m_a^-} (1 + \delta_{N,0}) (\mu_a + \mu_b - \mu_0) \times \sqrt{(2\ell_a + 1)(2\ell_b + 1)(L' - N)!(L - N)!} (\ell_a - \ell_b)(\ell_a + \ell_b)(\ell_a + \ell_b) \times C(1, 1, L; -\mu_a, -\mu_b, N) C(1, 1, L; -\mu_0, \mu_0, 0).
\] (6)

The index $N$ is limited by the restrictions imposed by the CG coefficients, i.e. $N = -m_a + m_b = -\mu_a + \mu_b$. Expression (4) has the advantage that the $F_{L N}^{\mu \nu}$ functions can be easily determined experimentally by performing measurements for a few orientations of the molecule with respect to the polarization direction. Note that, for a given photon energy, the $F_{L N}^{\mu \nu}$ functions only depend on the polar angle and the energy of the ejected electron. The dependence of the fully differential cross section with molecular orientation is entirely given by analytic Legendre and trigonometric functions. Hence, once the $F_{L N}^{\mu \nu}$ functions have been determined, the experiments can predict the electron angular distribution for any particular orientation. The $F_{00}^{\mu \nu}(\varepsilon, \theta_e)$ function is only accessible when $\theta_e$ is different from $0^\circ$ and $90^\circ$, and it gives access to the relative phase between the $^1\Sigma_u^+$ and $^1\Pi_u$ matrix elements (see equation (6)).

Integrating the fully differential cross section given in (4) over one or several angles and/or over electron or nuclear energies, different physical situations can be considered, each one representing a particular experimental condition [32]. In particular, integrating over the solid angle $\Omega_e$, leads to the cross section differential in the nuclear solid angle and in the energy of the ejected electron/ion irrespective of the electron emission direction
\[
\frac{d\sigma_{\mu_a=0}(\omega)}{d\Omega_e d\varepsilon_a} = \frac{1}{4\pi} \frac{d\sigma_{\mu_a=0}(\omega)}{d\varepsilon_a} [1 + \beta^{\mu_a}_{\alpha,\alpha}(\omega, \varepsilon_a) P_2(\cos \theta_n)].
\] (7)
where $P_2$ is the second-order Legendre polynomial, $d\sigma^{\mu_0}_a(\omega)/d\varepsilon_a$ is the cross section differential in the energy of the ejected electron

$$
\frac{d\sigma^{\mu_0}_a(\omega)}{d\varepsilon_a} = \frac{4\pi^2\omega}{3c} \sum_{\ell m \mu} |T_{a\ell m \mu}(\varepsilon_a)|^2
$$

and $\beta^{\mu_0}_{a,n}(\omega, \varepsilon_a)$ is the ionic asymmetry parameter

$$
\beta^{\mu_0}_{a,n}(\omega, \varepsilon_a) = \frac{3\mu_0^2 - 2}{2} \sum_{\ell m \mu} \frac{|T_{a\ell m \mu - M_i}(\varepsilon_a)|^2 [3(m_n - M_i)^2 - 2]}{\sum_{\ell m \mu} |T_{a\ell m \mu - M_i}(\varepsilon_a)|^2},
$$

where $M_i$ is the projection of the initial-state angular momentum. The above equations can also be used to obtain the cross sections differential in the energy of the residual molecular ion (nondissociative case) or the ejected proton (dissociative case) by using the energy conservation formula (3) that relates $\varepsilon_a$ to $W_{a\ell}$. Since the ground state of $H_2$ has $^1\Sigma_u^+$ symmetry, the dipole selection rule implies that only continuum states of $^1\Sigma_u^+$ and $^1\Pi_u$ symmetries can be populated. Hence, the cross section given in equation (8) can be written as the sum of $^1\Sigma_u^+$ and $^1\Pi_u$ cross sections:

$$
\frac{d\sigma^\mu_0_a(\omega)}{d\varepsilon_a} = \frac{d\sigma^\mu_0_a(\omega)}{d\varepsilon_a} + 2 \frac{d\sigma^\Pi_1_a(\omega)}{d\varepsilon_a}.
$$

Integrating equation (1) over the solid angle $\Omega_a$ leads to the cross section differential in the energy and solid angle of the ejected electron irrespective of the molecular orientation [33, 34]:

$$
\frac{d\sigma^{\mu_0}_a(\omega)}{d\varepsilon_a d\Omega_a} = \frac{1}{4\pi} \frac{d\sigma^{\mu_0}_a(\omega)}{d\varepsilon_a} [1 + \beta^{\mu_0}_{a,\ell}(\omega, \varepsilon_a) P_2(\cos \theta)],
$$

where $d\sigma^{\mu_0}_a(\omega)/d\varepsilon_a$ is the cross section differential in the energy of the ejected electron given in equation (8) and $\beta^{\mu_0}_{a,\ell}(\omega, \varepsilon_a)$ is the electron asymmetry parameter

$$
\beta^{\mu_0}_{a,\ell}(\omega, \varepsilon_a) = \frac{1}{5} \sum_{\ell m \mu} |T_{a\ell m \mu}(\varepsilon_a)|^2 \sum_{\mu, \ell b} \sum_{\ell a, \ell b} i(\ell_a - \ell_b) e^{i(\hat{n}_a(\varepsilon_a)-\hat{n}_b(\varepsilon_a))(-1)^{m_b+\mu_a}}
\times [(2\ell_a + 1)(2\ell_b + 1)]^{1/2} T^a_{\ell a \mu a \mu a}(\varepsilon_a) T_{\ell b \mu b \mu b}(\varepsilon_a) C(\ell_a, \ell_b, 2; -m_a, m_b, M_c)
\times C(\ell_a, \ell_b, 2; 0, 0, 0) C(1, 1, 2; -\mu_a, \mu_b, M_c) \delta_{m_a+\mu_a, m_b+\mu_b}.
$$

3. Wave functions

3.1. General treatment

Neglecting rotational effects, the initial wave function $\Psi_{gv}$ is evaluated in the adiabatic (Born–Oppenheimer (BO)) approximation

$$
\Psi_{gv}(\mathbf{r}, R) = R^{-1} \chi_v(R) \psi_g(\mathbf{r}, R),
$$

where $\psi_g$ and $\chi_v$ are the usual electronic and nuclear BO wave functions [20]. As shown in [19, 35], when doubly excited states participate in the ionization process, the final wave function $\Psi^{-}_{avu \ell a m a \varepsilon a}$ cannot be expressed in such a simple way. Let us call $\phi_r(\mathbf{r}, R)$ the doubly
excited states of energy $E_r(R)$, and $\psi_{a_1}^{0_1}(r, R)$ the nonresonant electronic continuum states in which the former are embedded. As in [19], we will assume that $\psi_{a_1}^{0_1}(r, R)$ represents asymptotically an electron in a molecular state with the correct symmetry of the residual molecular ion and the other electron in a continuum state with the proper incoming boundary conditions. In this case, the wave function $\Psi_{a_1}^{0_1}(r, R)$ associated with the $\alpha$ electronic state of the residual molecular ion must be written [19, 35]:

$$\Psi_{a_1}^{0_1}(r, R) = \sum_{r'} \phi_r(r, R) \xi_{a_1}^{r'}(r) + \psi_{a_1}^{0_1}(r, R) \chi_{r'}(R)$$

$$+ \lim_{\eta \to 0} \sum_{r'} \sum_{\alpha'} \sum_{\ell} \sum_{\ell'} \int \frac{dE_{r'}}{E_r - E_{r'} + i\eta}$$

$$\times \int dR' V_{a_1}^{r'}(r) \xi_{a_1}^{r'}(r, R) \psi_{a_1}^{0_1}(r, R) \chi_{r'}(R),$$

(14)

where

$$V_{a_1}^{r'}(r) = \langle \phi_r | H_{a_1} | \psi_{a_1}^{0_1} \rangle \chi_{r'}(R)$$

(15)

with $H_{a_1}$ the electronic Hamiltonian and $E_a = \varepsilon_a + W_{r'\alpha}$. Note that we have dropped the index $m_\alpha$ because $1 \Sigma^+$ and $1 \Pi$ continuum states, which have different $m_\alpha$’s, are not coupled. In equations (14) and (15), $\chi_{r'}$ is the nuclear wave function solution of

$$[T(r) + E_a(r) - W_{r'\alpha}] \chi_{r'}(R) = 0,$$

(16)

where $E_a(r)$ is the potential energy curve associated with the $\alpha$ electronic state of the residual molecular ion, $W_{r'\alpha}$ is the energy of the residual molecular ion and $\xi_{a_1}^{r'}$ is the solution of [19, 36, 37]

$$[E_a - E_r(r) - T(r)] \xi_{a_1}^{r'}(r) = V_{a_1}^{r'}(r) + \lim_{\eta \to 0} \sum_{r'} \sum_{\alpha'} \sum_{\ell} \sum_{\ell'} \int \frac{dE_{r'}}{E_r - E_{r'} + i\eta}$$

$$\times \int dR' V_{a_1}^{r'}(r, R) \xi_{a_1}^{r'}(r, R).$$

(17)

The latter equation represents nuclear motion when the electrons are in the quasistationary state $\phi_r$. The matrix element in equation (15) represents the coupling between the resonance $\phi_r$ and the nonresonant wave function $\psi_{a_1}^{0_1}$ and vibrational state $\chi_{r'}$. Hence, the two terms on the right-hand side of equation (17) are the result of the autoionizing character of the $\phi_r$ state and represent its decay to the adjacent electronic continuum. The last term, as well as the last one in equation (14), is nonlocal due to the presence of the $\xi_{a_1}^{r'}$ functions, and it can be split into a $\delta$-function term and a principal value term. Therefore, $\xi_{a_1}^{r'}$ takes into account the variation of the nuclear motion due to transition from a resonant to a nonresonant electronic state associated with different potential energy curves. In applying equations (14) and (17), we have excluded the bound electronic states because contributions from the latter to the ionization process are expected to be negligible.

Equations (14) and (17) are exact within the adiabatic approximation [19, 37]. In this approximation,

$$P \psi_{a_1}^{0_1}(r, R) = \psi_{a_1}^{0_1}(r, R) \chi_{r'}(R),$$

(18)

New Journal of Physics 11 (2009) 043020 (http://www.njp.org/)
where $P$ is a projector given by
\[
P = 1 - \sum_{\nu'} |\phi_\nu'(\mathbf{r}, \mathbf{R})\rangle \langle \phi_\nu'(\mathbf{r}, \mathbf{R})|,
\]
and $P\psi_{\alpha\nu_0 \ell_0 \epsilon_0}^0$ is the nonresonant scattering wave function that satisfies the equation
\[
\{P[T(R) + \mathcal{H}_0]P - E_\alpha\} P\psi_{\alpha\nu_0 \ell_0 \epsilon_0}^0(\mathbf{r}, \mathbf{R}) = 0. \tag{20}
\]

### 3.2. Boundary conditions compatible with the full determination of the proton momentum

When the boundary conditions imposed by the experiment are not consistent with equation (18), i.e. when $P\psi_{\alpha\nu_0 \ell_0 \epsilon_0}^0(\mathbf{r}, \mathbf{R})$ cannot be written as the product of an electronic molecular state and a vibrational state, the above formalism must be slightly modified. This is the case when the measurement does not respect the molecular symmetry of the electronic wave function $\psi_{\alpha\nu_0 \ell_0 \epsilon_0}^0$. In the next section, we will compare electron angular distributions for dissociative photoionization of $\mathrm{H}_2$ and $\mathrm{D}_2$ with those obtained in COLTRIMS experiments in which the momentum of the emitted proton is unambiguously determined. These experiments are able to separate events in which dissociative ionization leads to $\mathrm{H}^+ + \mathrm{H}$ from those in which it leads to $\mathrm{H} + \mathrm{H}^+$ (i.e. in which the proton goes to the left and the hydrogen atom to the right or vice versa) for the same energy of the proton. In other words, by measuring the full momentum of the ejected proton and not only the energy, the measurement does not respect the inversion symmetry of the molecule. As we will discuss below, this has no practical consequence when ionization occurs between the first and the second ionization thresholds of $\mathrm{H}_2$. However, above the second ionization threshold, the above theory must reproduce the fact that the proton is emitted in a well-defined direction and the residual atom is ejected in the opposite direction.

Formally, this means that the final nonresonant scattering wave function, $P\psi_{\alpha\nu_0 \ell_0 \epsilon_0}^0$, solution of equation (20), must now behave asymptotically as
\[
P\psi_{\alpha\nu_0 \ell_0 \epsilon_0}^0(\mathbf{r}, \mathbf{R}) \xrightarrow{R \to \infty} \Theta \left[ \psi_{1s\ell}(\mathbf{r}_1) \psi_{\ell_0 \epsilon_0}(\mathbf{r}_2) \right] \chi_{\nu_0}(R)
\]
\[
\equiv \frac{1}{\sqrt{2}} \Theta \left[ \left( \psi_{1s\sigma_g}(\mathbf{r}_1) + \psi_{1s\sigma_u}(\mathbf{r}_1) \right) \psi_{\ell_0 \epsilon_0}(\mathbf{r}_2) \right] \chi_{\nu_0}(R), \tag{21}
\]
or
\[
P\psi_{\beta\nu_\beta \ell_\beta \epsilon_\beta}^0(\mathbf{r}, \mathbf{R}) \xrightarrow{R \to \infty} \Theta \left[ \psi_{1s\ell}(\mathbf{r}_1) \psi_{\ell_\beta \epsilon_\beta}(\mathbf{r}_2) \right] \chi_{\nu_\beta}(R)
\]
\[
\equiv \frac{1}{\sqrt{2}} \Theta \left[ \left( \psi_{1s\sigma_g}(\mathbf{r}_1) - \psi_{1s\sigma_u}(\mathbf{r}_1) \right) \psi_{\ell_\beta \epsilon_\beta}(\mathbf{r}_2) \right] \chi_{\nu_\beta}(R), \tag{22}
\]
where $\Theta$ is the symmetrization (antisymmetrization) operator for singlet (triplet) states, $\psi_{1s\ell}$ and $\psi_{1s\ell}$ are the wave functions representing the $1s$ orbital of the hydrogen atoms $A$ and $B$, respectively, $\psi_{\ell_0 \epsilon_0}$ is the asymptotic form of the continuum wave function representing the escaping electron, and $\psi_{1s\sigma_g}$ and $\psi_{1s\sigma_u}$ are the wave functions representing the $1s\sigma_g$ and $2p\sigma_u$
orbits of $H_2^+$ at infinite internuclear distance:

$$
\psi_{1s_\sigma}^\infty = \frac{1}{\sqrt{2}} (\psi_{1s_\tau} + \psi_{1s_\pi}),
$$  

$$
\psi_{2p_\sigma}^\infty = \frac{1}{\sqrt{2}} (\psi_{1s_\tau} - \psi_{1s_\pi}).
$$  

In equation (21), one of the electrons is associated with a proton labelled $A$ producing the emission of a hydrogen atom $A$ in the ground state $1s$ in a given direction (let us say left), whereas, in equation (22), the emission occurs in the other direction (to the right). The vibrational wave function $\chi_{v_\ell}^\infty (R)$ describes the relative motion of the proton and the hydrogen atom in the asymptotic limit $R \to \infty$. The boundary conditions defined by (21) and (22) imply that, in the adiabatic approximation, the nonresonant state cannot be written as in equation (18). Instead we will write

$$
P \psi_{A(B)\ell_{A,B} \epsilon_{A,B} \ell_{A,B}}^- = \frac{1}{\sqrt{2}} \left[ \psi_{1s_\sigma \ell_{u} \ell_{g}}^0 (r, R) \chi_{v_\ell \sigma}^\infty (R) \pm \psi_{2p_\sigma \ell_{u} \epsilon_{A,B} \ell_{A,B}}^0 (r, R) \chi_{v_\ell \epsilon_{A,B}}^\infty (R) \right],
$$

where $\psi_{1s_\sigma \ell_{u} \ell_{g}}^0$ and $\psi_{2p_\sigma \ell_{u} \epsilon_{A,B} \ell_{A,B}}^0$ are solutions of the equation

$$
P \mathcal{H}_{\ell \epsilon} P \psi_{\alpha \ell_{A,B} \epsilon_{A,B}}^0 = (\mathcal{E}_\alpha (R) + \epsilon_{A,B}) P \psi_{\alpha \ell_{A,B} \epsilon_{A,B}}^0,
$$

with $\alpha = 1s_\sigma$ and $2p_\sigma$, and $\mathcal{E}_\alpha (R) = \mathcal{E}_{1s_\sigma} (R)$ and $\mathcal{E}_\alpha (R) = \mathcal{E}_{2p_\sigma} (R)$, respectively. Equation (25) implies that the $P$ projector can be written as the sum of two orthogonal projection operators associated with the $1s_\sigma$ and $2p_\sigma$ ionization thresholds, i.e. $P = P_{1s_\sigma} + P_{2p_\sigma}$. Note that, in equation (25), the boundary conditions defined in (21) and (22) are fulfilled if

$$
\begin{align*}
\chi_{v_\ell \sigma}^\infty (R) & \quad \rightrightarrows_{R \to \infty} \chi_{\ell_{A,B} \epsilon_{A,B}}^\infty (R), \\
\chi_{v_\ell \epsilon_{A,B}}^\infty (R) & \quad \rightrightarrows_{R \to \infty} \chi_{\ell_{A,B} \epsilon_{A,B}}^\infty (R)
\end{align*}
$$

and

$$
\begin{align*}
\psi_{1s_\sigma \ell_{u} \ell_{g}}^0 & \quad \rightrightarrows_{R \to \infty} \Theta \left[ \psi_{1s_\sigma \ell_{u} \ell_{g}}^\infty (r_1) \psi_{\ell_{A,B} \epsilon_{A,B}}^\infty (r_2) \right], \\
\psi_{2p_\sigma \ell_{u} \epsilon_{A,B} \ell_{A,B}}^0 & \quad \rightrightarrows_{R \to \infty} \Theta \left[ \psi_{2p_\sigma \ell_{u} \epsilon_{A,B} \ell_{A,B}}^\infty (r_1) \psi_{\ell_{A,B} \epsilon_{A,B}}^\infty (r_2) \right].
\end{align*}
$$

These conditions are only fulfilled if the short-range non-Coulomb phase shifts in the $1s_\sigma$ and $2p_\sigma$ ionization channels are identical. This is a reasonable approximation except for very small electron energies; hence equation (25) is a reasonable approximation whenever the BO approximation is a good approximation.

The $V_{\alpha \ell_{A,B} \epsilon_{A,B}}^r$ matrix element given by equation (15) now takes the form

$$
\begin{align*}
V_{A(B)\ell_{A,B} \epsilon_{A,B} \ell_{A,B}}^r & = \frac{1}{\sqrt{2}} \left[ \langle \phi_r | \mathcal{H}_{\ell \epsilon} P_{1s_\sigma} | \psi_{1s_\sigma \ell_{u} \ell_{g}}^0 \rangle \chi_{v_\ell \sigma}^\infty (R) \pm \langle \phi_r | \mathcal{H}_{\ell \epsilon} P_{2p_\sigma} | \psi_{2p_\sigma \ell_{u} \epsilon_{A,B} \ell_{A,B}}^0 \rangle \chi_{v_\ell \epsilon_{A,B}}^\infty (R) \right] \\
& = \frac{1}{\sqrt{2}} \left[ V_{1s_\sigma \ell_{u} \ell_{g}}^r \pm V_{2p_\sigma \ell_{u} \epsilon_{A,B} \ell_{A,B}}^r \right].
\end{align*}
$$

New Journal of Physics 11 (2009) 043020 (http://www.njp.org/)
Note that there are no mixed terms \( P_{1\sigma_g} P_{2\rho_u} \) because these projectors are orthogonal. Hence, the vibrational state \( \xi_{1\sigma_g,E_g}^r (R) \) solution of equation (17) can now be written as

\[
[E_{A(B)} - E_r (R) - T (R)] \xi_{A(B),1\sigma_g,E_{A(B)}}^r (R) = \frac{1}{\sqrt{2}} [V^r_{1\sigma_g,\ell_g} E_g (R) \pm V^r_{2\rho_u,\ell_u} E_u (R)] + \lim_{\eta \rightarrow 0} \sum_{\alpha'} \sum_{\ell'_g} \sum_{\ell'_u} \int dE'_\alpha' E'_\alpha' \frac{V^r_{\alpha',\ell'_g,\ell'_u} E'_\alpha'}{E'_\alpha' - E'_\alpha + i\eta} \int V^r_{\alpha',\ell'_g,\ell'_u} E'_\alpha' (R') \xi_{\alpha,\ell_g,\ell_u}^r E_u (R') dR'.
\] (30)

If one neglects second-order mixed terms \( V^r_{1\sigma_g,\ell_g} E_g \) \( V^r_{2\rho_u,\ell_u} E_u \) in the last line of the previous equation, the solution of equation (30) can be written as

\[
\xi_{A(B),1\sigma_g,E_{A(B)}}^r (R) = \frac{1}{\sqrt{2}} [\xi_{1\sigma_g,\ell_g,E_g}^r \pm \xi_{2\rho_u,\ell_u,E_u}^r],
\] (31)

where \( \xi_{1\sigma_g,\ell_g,E_g}^r \) and \( \xi_{2\rho_u,\ell_u,E_u}^r \) are independent solutions of equation (17) for the \( 1\sigma_g \) and \( 2\rho_u \) ionization thresholds, respectively.

Similarly, the total wave function with the desired boundary conditions can be written as

\[
\Psi^{-}_{1\sigma_g,1\sigma_g,\ell_g,\ell_g,E_{A(B)}} (r, R) = \frac{1}{\sqrt{2}} \left[ \sum_{r'} \phi_{r'} (r, R) \xi_{1\sigma_g,\ell_g,E_g}^r (R) \right.
\]
\[
\left. \pm \sum_{r'} \phi_{r'} (r, R) \xi_{2\rho_u,\ell_u,E_u}^r (R) + \psi_{1\sigma_g,\ell_g,E_g}^{0-} (r, R) \chi_{1\sigma_g,E_g} (R) \right.
\]
\[
\left. \pm \psi_{2\rho_u,\ell_u,E_u}^{0-} (r, R) \chi_{2\rho_u,E_u} (R) + \lim_{\eta \rightarrow 0} \sum_{r'} \sum_{\ell'_g} \sum_{\ell'_u} \int dE'_\alpha' E'_\alpha' \frac{1}{E'_\alpha' - E'_\alpha + i\eta} \right.
\]
\[
\times \int dR' V^r_{\alpha',\ell'_g,\ell'_u} E'_\alpha' (R') \xi_{1\sigma_g,\ell_g,E_g}^r (R') \psi_{\alpha',\ell'_g,\ell'_u}^{0-} (r, R) \chi_{\ell'_u,E_u} (R')
\]
\[
\left. \pm \lim_{\eta \rightarrow 0} \sum_{r'} \sum_{\ell'_g} \sum_{\ell'_u} \int dE'_\alpha' E'_\alpha' \frac{1}{E'_\alpha' - E'_\alpha + i\eta} \right.
\]
\[
\times \int dR' V^r_{\alpha',\ell'_g,\ell'_u} E'_\alpha' (R') \xi_{2\rho_u,\ell_u,E_u}^r (R') \psi_{\alpha',\ell'_g,\ell'_u}^{0-} (r, R) \chi_{\ell'_u,E_u} (R'),
\] (32)

which can be simply written as a combination of the solutions that one would obtain with boundary conditions that preserve the \( g \) and \( u \) symmetries:

\[
\Psi^{-}_{1\sigma_g,1\sigma_g,\ell_g,\ell_g,E_{A(B)}} (r, R) = \frac{1}{\sqrt{2}} \left[ \Psi_{1\sigma_g,\ell_g,E_g}^{-} (r, R) \pm \Psi_{2\rho_u,\ell_u,E_u}^{-} (r, R) \right].
\] (33)

Thus, in practice, one has to solve the same equations as described in the previous section for the case in which the molecular symmetry is preserved in the measurement. But then one has to combine them as indicated in equation (33) to properly account for the specific boundary conditions in the COLTRIMS experiment.
3.3. Computational methods

The computational methods used to obtain the wave functions included in the $T_{\alpha\ell m \mu}(\varepsilon)$ matrix elements have been described in detail in previous work [20, 38]. Briefly, the vibrational (bound and dissociative) wave functions have been expanded in a basis of 240 B-splines of order $k = 8$ contained in a box of 12 au. The electronic ground state $\Psi_g$ results from a configuration interaction (CI) calculation in which the $H_2$ Hamiltonian has been diagonalized in a basis of 321 configurations built from products of one-electron $H_2$ orbitals and pseudo-orbitals. The calculated electronic energy, at the equilibrium internuclear distance, $R = 1.4$ au, is $-1.886\,5023$ au, to be compared with the exact non relativistic value $-1.888\,761\,38$ au [39]. All these orbitals have been represented through a one-centre expansion that includes spherical harmonics up to $\ell = 11$. The corresponding radial parts have been expanded in a basis of 160 B-splines of order $k = 8$ in a box of radial length of 60 au. The final electronic continuum state $\Psi_{\alpha \nu u \ell a, \ell a, \mu}$ results from a close coupling calculation that includes all partial waves with $\ell \leq 7$ associated with the two lowest ionization thresholds of $H_2$: $X^2\Sigma_g^+(1s\sigma_g)$ and $^2\Sigma_u^+(2p\sigma_u)$. For every value of $R$, these continuum states satisfy the usual incoming boundary conditions corresponding to (i) one electron in a bound electronic state of $H^+_2$ and (ii) the other electron in a single outgoing spherical wave with a well-defined value of the angular momentum $\ell$ and a combination of incoming spherical waves for all accessible electronic states of $H^+_2$ and all possible values of the angular momentum of the ejected electron compatible with the molecular symmetry [20] (for a given energy, there is a continuum state for each electronic state $\alpha$ of the residual $H^+_2$ ion and angular momentum $\ell$ of the ionized electron). Therefore, all calculated wave functions include electron correlation and the two-centre character of molecular potential. In addition, $\Psi_{\alpha \nu u \ell a, \ell a, \mu}$ accounts for interferences among the various ionization thresholds and angular momenta of the ejected electron.

4. Results

We will present results at photon energies 20, 27 and 33 eV. At 20 eV, autoionizing doubly excited states are barely populated since even the lowest $Q_1$ state lies well outside the FC region (see figure 1). At 27 eV, the $Q_1$ states are significantly populated [17, 18, 42]. These states are between the first and the second ionization thresholds and, consequently, they can only autoionize by leaving the residual $H^+_2$ ion in the ground $^2\Sigma_u^+(1s\sigma_g)$ electronic state. Depending on the energy carried by the nuclei, the molecular ion can remain in a bound vibrational state or can dissociate leading to $H + H^+$. At a photon energy of 33 eV, the $Q_2$ doubly excited states can be populated. These states lie above the second ionization threshold and, therefore, can decay by leaving $H^+_2$ in the $^2\Sigma_g^+(1s\sigma_g)$ or $^2\Sigma_u^+(2p\sigma_u)$ states. The latter $H^+_2$ state is completely dissociative (see figure 1) and is degenerate with the $^2\Sigma_g^+(1s\sigma_g)$ one at $R \to \infty$. At much higher photon energies (>40 eV) doubly excited states of the $Q_3$ and higher series can also be populated [41], but their contribution to the dissociative ionization spectrum is very small [23].

4.1. $h\omega = 20$: direct ionization

Photoionization of $H_2$ leading to $H^+_2$ in the $X^2\Sigma_g^+$ state has been extensively studied both experimentally and theoretically. Total photoionization cross sections have been measured since the 1960s [43]–[47] and theoretical calculations have generally agreed well with them [48]–[51].

New Journal of Physics 11 (2009) 043020 (http://www.njp.org/)
Figure 1. Potential energy curves of the $H_2$ and $H_2^+$ systems. The shaded area represents the ionization continuum. The different series of doubly excited states, $Q_n$, are represented by different colours: red lines, $Q_1$ states; blue lines, $Q_2$ states; orange lines, $Q_3$ states; green lines, $Q_4$ states. $Q_n$ states of $^1\Pi_u$ symmetry are represented by full lines and those of $^1\Sigma_u^+$ symmetry by dashed lines. At large internuclear distances, the $Q_1$ states dissociate into $H(n=1) + H(n \geq 2)$, and the $Q_2$, $Q_3$ and $Q_4$ states into $H(n=2) + H(n \geq 2)$. Numerical data are taken from [35, 40, 41]. The FC region, which corresponds to the classical turning points of the vibrational ground state, is enclosed by the two vertical dashed lines. The energy origin is placed on the lowest rovibrational level of the ground electronic state of $H_2$. The three horizontal dashed lines indicate the three photon energies considered in this work.

As mentioned above, at a photon energy of 20 eV, the only open channel is the $^2\Sigma_u^+(1s\sigma_g)$ one and the contribution from doubly excited states is expected to be very small. Therefore, the photoelectron angular distributions presented in this subsection will be a good reference to investigate in the next subsections the effect of the doubly excited states in the angular distributions.

Figure 2 shows schematically the different physical processes that compete in this energy range: (i) nonresonant nondissociative photoionization

$$H_2 + h\omega \rightarrow H_2^+ (1s\sigma_g, \nu) + e^- \quad (34)$$

and (ii) nonresonant dissociative photoionization

$$H_2 + h\omega \rightarrow H_2^+ (1s\sigma_g) + e^- \rightarrow H(n\ell) + H^+ + e^- \quad (35)$$
Figure 2. Pathways for ionization of $\text{H}_2$ by absorption of a 20 eV photon. The figure shows the ground electron state of $\text{H}_2$, and the first two ionization thresholds $X^2\Sigma_g^+ (1s\sigma_g)$ and $^2\Sigma_u^+(2p\sigma_u)$. The thick vertical line represents a 20 eV vertical transition from the ground state; the dashed part of this line indicates the excess photon energy. The maximum energy that the ejected electron can carry when the residual $\text{H}_2^+$ ion dissociates (following the full orange line superimposed to the $X^2\Sigma_g^+ (1s\sigma_g)$ curve) is indicated by $\varepsilon_1$. For completeness, the figure also shows the lowest $Q_1$ and $Q_2$ doubly excited states of $^1\Pi_u$ (full lines) and $^1\Sigma_u^+$ (dashed lines) symmetries.

In the first case, the residual molecular ion can remain in different bound vibrational states. This is the dominant mechanism in the ionization process at this and higher photon energies [52]. At low photon energies, the relative population of the $\text{H}_2^+$ vibrational states closely follows an FC distribution. The contribution of the dissociative process to the total photoionization cross section is smaller than 5%, depending on photon energy [20]. In spite of this, dissociative ionization is the process that has more experimental interest since determination of the momentum of the ejected proton allows one to unambiguously determine the orientation of the $\text{H}_2$ molecule at the instant of ionization.

Figure 3 displays the $\text{H}_2$ and $\text{D}_2$ KER spectra, i.e. the cross sections integrated over electron emission angle as functions of the proton kinetic energy, for molecules at 0°, 54.7° and 90° with respect to the polarization direction (see equations (7) and (11)). As can be seen, the results are rather insensitive to the orientation of the molecule. The cross sections decrease almost
Figure 3. Cross section integrated over electron emission angle as a function of electron (proton) energy for $\text{H}_2$ (black line) and $\text{D}_2$ (red dashed line) and for the three following orientations of the polarization vector with respect to the molecular axis: (a) $\theta_n = 0^\circ$, (b) $\theta_n = 54.7^\circ$ and (c) $\theta_n = 90^\circ$. All results are obtained at $\bar{\hbar}\omega = 20$ eV.

exponentially with proton and deuteron energies, which is a consequence of the exponential decay of the corresponding FC factor. This is the typical behaviour associated with direct (non resonant) dissociative ionization. As can be seen from the figures, direct ionization mainly leads to slow protons with approximately less than 1 eV. The cross sections for $\text{D}_2$ are $\sim 3$ times smaller, which reflects the fact that the effective FC region is narrower for $\text{D}_2$ than for $\text{H}_2$.

As described in the previous section, the electron angular distributions are fully determined at any molecular orientation if one knows the $F_{0 L N}^{\mu_0}$ coefficients as a function of polar emission angle $\theta_e$ and electron energy $\epsilon$ (viz the reverse of the proton kinetic energy according to equation (3)). Figure 4 displays the results for the $F_{0 L N}^{\mu_0}$ coefficients integrated over the electron energy associated with the dissociative process as a function of $\theta_e$. We note that, for the photon energy considered in this subsection, the $F_{0 L N}^{\mu_0}$ coefficients obtained at different electron energies exhibit patterns similar to those displayed in figure 4 (the only visible difference is an overall scaling factor). The $F_{000}^{0}$ coefficient depends slightly on the polar emission angle, since this function is described mainly by the first coefficient $C_{000}^{0} (\epsilon) P_{0}^{0} (\cos \theta_e)$ given by equation (5), with a minor contribution from the second coefficient (note that $P_{0}^{0} (\cos \theta_e) = 1$). The $F_{20}^{0}$ coefficient exhibits a stronger dependence on the emission angle, and this can also be understood by the first coefficient of the expansion $C_{020}^{0} (\epsilon) P_{2}^{0} (\cos \theta_e)$. The same reasonings apply to the $F_{21}^{0}$ and $F_{22}^{0}$ coefficients, which reflect the fact that all these functions are mainly described by the contribution of the first partial wave $\ell = 1$.

Very recently, Lafosse et al [4] have determined the $F_{0L N}^{0}$ coefficient by collecting electrons in the $[0, 2]$ eV energy range. These results are also included in figure 4. Note that the sign of our $F_{21}^{0}$ coefficient has been changed (panel (c)) due to the different choice of the Condon–Shortley factor in the definition of the spherical harmonics [53]. The experimental results are renormalized to a single value of the theoretical $F_{00}^{0}$ function at $\theta_e = 0^\circ$. As can be seen, the agreement is excellent. The $F_{0 L N}^{\mu_0}$ coefficients for the $\text{D}_2$ molecule (not shown) exhibit similar patterns, but they are $\sim 3$ times smaller (as in the case of the cross sections shown in figure 3).
Figure 4. Comparison between the calculated and the measured $F_{LN}(\theta_e)$ coefficients for H$_2$ obtained for a photon energy of 20 eV. (a) $F_{00}(\theta_e)$, (b) $F_{20}(\theta_e)$, (c) $F_{21}(\theta_e)$ and (d) $F_{22}(\theta_e)$. Black full lines, theoretical calculations; red square symbols presented with error bars, experimental results obtained in [4]. Since we are comparing with relative measurements, we have plotted the dimensionless coefficients $F_{\mu_0}^{\mu}(\omega,\varepsilon,\theta_e) = (4\pi/\sigma)F_{\mu_0}^{\mu}(\omega,\varepsilon,\theta_e)$, where $\sigma$ is the cross section integrated over electron emission angle $\sigma(\omega,\varepsilon) = 2\pi \int_0^\pi F_{00}^{\mu}(\omega,\varepsilon,\theta_e)\sin\theta_e\,d\theta_e$.

Figure 5 shows the electron angular distributions integrated over the whole electron energy range, for $\theta_n = 0^\circ$, 54.7° and 90°, and $\phi_n = 0$ (we consider the polarization vector contained in the $x$–$z$ molecular plane). In all cases, electron emission is mainly produced along the polarization axis, with a shape that is similar to a p wave. This reflects the fact that the ionization process is mainly described by the first partial wave $\ell = 1$. Similar conclusions were obtained in [29] for the same photon energy in the fixed nuclei approximation. Experimental angular distributions [4, 54] exhibit similar patterns.

To complete the study of the angular distribution at 20 eV, we present the results obtained for the proton and the electron angular distributions corresponding to a distribution of randomly oriented molecules. As explained previously, the study of these parameters gives less physical information than the analysis of the angular distributions arising from fixed-in-space molecules. However, the beta parameters are much easier to determine experimentally and contain very simple physical information. The electronic $\beta_e$ parameter reflects the partial wave composition, whereas the nuclear $\beta_n$ parameter gives the relative weights of the $\Sigma_g^+ \rightarrow \Sigma_u^+$ and $\Sigma_g^+ \rightarrow \Pi_u$ transitions. The value of electron beta parameter, $\beta_e$, is expected to be 2 in the united atom limit, and hence deviations from 2 are understood in terms of the molecular field felt by the photoelectron. In practice, the principal effect of the molecular field is to populate partial waves with $\ell > 1$.  

New Journal of Physics 11 (2009) 043020 (http://www.njp.org/)
Figure 5. Electron angular distributions of H$_2$ integrated over electron energy for the following three orientations of the molecular axis with respect to polarization direction: (a) $\theta_n = 0^\circ$, (b) $\theta_n = 54.7^\circ$ and (c) $\theta_n = 90^\circ$. The numbers at the bottom are the values at the maximum of the angular distribution. Panel (d) displays the coordinate system used throughout the paper. All results are obtained at $\hbar\omega = 20$ eV.

In the left panel of figure 6, we present the photoelectron beta parameter as a function of the electron kinetic energy for both H$_2$ and D$_2$. Electrons with energies larger than $\sim 2$ eV are associated with the formation of bound vibrational states of H$_2^+(\nu)$ (nondissociative process). In all cases, the value of the beta parameter is very close to 2 and monotonically decreases with electron energy. The figure also shows the electron angular distribution with respect to the polarization vector for $\beta_e \sim 2$. Lafosse et al [4] measured a value of $\beta_e \approx 1.7 \pm 0.1$ at a photon energy of 20.0 eV, where Hikosaka and Eland [54] measured $\beta_e \approx 1.83 \pm 0.05$ and Eland et al [55] $\beta_e \approx 1.95 \pm 0.1$ both at a photon energy of 21.2 eV. In order to compare with the previous experimental results, in which the angular distribution was not resolved in electron energy, one has to integrate the differential cross sections defined in equation (7) over electron energy. One can thus define an ‘integrated’ beta parameter by assuming that the angular distribution integrated over electron energy also follows a formula similar to that of equation (7). For the H$_2$ ‘integrated’ beta parameter associated with the dissociative process (electrons with energy less than $\sim 2$ eV) we obtain 0.42, whereas for the beta parameter associated with the nondissociative process (i.e. producing bound vibrational states) we obtain 1.93. The total beta parameter takes a value of 1.90, which agrees with the previous experimental values. Similar results are obtained for D$_2$.

The proton and deuteron angular distributions for H$_2$ and D$_2$ molecules are shown in the right panel of figure 6 as a function of the proton and deuteron kinetic energies, respectively. The value of this parameter slightly oscillates with proton energy. This is due to the small contribution of the Q$_1$ $^1\Sigma_u^+$ doubly excited states. This is clearly proved by calculations in which the doubly Q$_1$ states are excluded: the resulting parameter varies monotonically with proton energy. The ionic asymmetry parameter takes values around $\sim 0.1$, which implies that the $^1\Sigma_u^+$ symmetry slightly dominates over the $^1\Pi_u$ one (see equation (7)). Similar oscillations are also observed in the D$_2$ molecule. In figure 6, we have also plotted the proton angular distribution for
Electron asymmetry parameter
\[ D_2 \]
\[ H_2 \]
\[ \text{noiger evitaicossid-noN} \]
\[ \varepsilon \]
\[ A \]
\[ B \]

Proton asymmetry parameter
\[ H_2 \]
\[ D_2 \]
\[ \text{noitubirtnoc tnanoser noN} \]
\[ \varepsilon \]

Figure 6. Left panel, electron asymmetry parameter as a function of electron energy. The vertical dashed lines indicate the threshold for nondissociative ionization. The lobe represents the angular distribution for \( \beta_e = 2 \). Right panel, nuclear asymmetry parameter as a function of proton and deuteron energy. The lobes represent the ion angular distributions obtained at the proton energies labelled by the symbols \( A \) and \( B \). The non-resonant contribution is indicated by dotted lines. In all panels, full black and dashed red lines correspond to \( H_2 \) and \( D_2 \), respectively. All results are obtained at \( \hbar \omega = 20 \text{ eV} \).

\[ \beta_h = 0.1 \text{ and } 0.2, \text{ i.e. for slow and fast protons, respectively. The experimental results are scarcer than for the electron beta parameter. Lafosse et al} [4] \] have measured a value of \( \beta_{H^+} \approx 0 \pm 0.1 \) for a photon energy of 20.0 eV, where Hikosaka et al [54] have found a value of \( \beta_{H^+} \approx 0.2 \pm 0.05 \) and Eland et al [55] a value of \( \beta_{H^+} \approx 0.14 \pm 0.1 \) for a photon energy of 21.2 eV. The ‘integrated’ ionic asymmetry parameter takes a value of 0.073 for \( H_2 \) and 0.068 for \( D_2 \), which agree well with the previous experimental results.

In conclusion, for randomly oriented molecules, the electrons strongly prefer to be emitted along the electric vector, while \( H^+ \) emission is relative isotropic.

4.2. \( \hbar \omega = 27 \): the role of the \( Q_1 \) doubly excited states.

At this photon energy, it is already possible to populate the \( Q_1 \) doubly excited states (see figure 1). Energy positions and autoionization widths are known from previous theoretical work (see e.g. [35, 56, 57] and references therein). The resonance parameters resulting from the \( Q_1 \) wave functions calculated in the present work are in excellent agreement with those of Tennyson [57] and Sánchez and Martín [35]. Only quite recently [19, 52] was it possible to explain the role of these resonant states in dissociative photoionization, showing that the coupling between the resonant and nonresonant amplitudes was responsible for several peaks observed in the experimental work [16, 17, 42]. The processes that can contribute to dissociative ionization are

\[ H_2(X^1\Sigma_g^+) + \hbar \omega \rightarrow H_2^+ (1s\sigma_g) + e^- \rightarrow H^+ + H(1s) + e^- \]  \hspace{1cm} (36)

\[ \rightarrow H_2^{*+}(Q_{1\Pi_u}) \rightarrow H_2^+ (1s\sigma_g) + e^- \rightarrow H^+ + H(1s) + e^- \]  \hspace{1cm} (37)

\[ \rightarrow H_2^{*+}(Q_{1\Pi_u}) \rightarrow H_2^+ (1s\sigma_g) + e^- \rightarrow H^+ + H(1s) + e^- . \]  \hspace{1cm} (38)

New Journal of Physics 11 (2009) 043020 (http://www.njp.org/)
Figure 7. Semiclassical pathways for dissociative ionization by absorption of a 27 eV photon. (a) Nonresonant ionization leading to H$_2^+$ (1s$_g$) (equation (36) in the text). (b) Resonant ionization through the lowest Q$_1$ doubly excited states leading to H$_2^+$ (1s$_g$) (equation (37) in the text). Red and blue lines represent the first Q$_1$ and Q$_2$ resonant states, respectively, taken from [35, 40], with symmetry $^1\Pi_u$ (full lines) and $^1\Sigma_u^+$ (dashed lines). The thick vertical line represents a 27 eV vertical transition from the ground state; the dashed part of this line indicates the excess photon energy. The energy carried by the autoionized electron when the residual H$_2^+$ ion dissociates (following the full orange line superimposed to the curves of the lowest Q$_1$ state and the X$^2\Sigma_g^+$ (1s$_g$) threshold) is indicated by $\varepsilon_2$. In this figure, autoionization is supposed to occur at $R = 2.5$ au. From the figure, the KER is approximately given by the difference between K$_2$ (the kinetic energy of the dissociating H$_2$ molecule in the Q$_1$ state at $R = 2.5$ au) and D$_1$ (the energy required to dissociate H$_2^+$ at $R = 2.5$ au).

The left panel of figure 7 illustrates the direct dissociative ionization process given in equation (36), which is similar to that described in the previous section. Simultaneously to this direct process, the Q$_1$ resonant states are populated and, after some time, they autoionize leading to the delayed emission of an electron and to a dissociative H$_2^+$ nuclear state (right panel of figure 7). It is important to note that autoionization can occur well outside the FC region and in a large range of internuclear distances.

In figure 8, we present the calculated KER spectrum (i.e. the cross section integrated over the electron emission angle as a function of the proton kinetic energy) for $\theta_n = 0^\circ$, 54.7$^\circ$ and 90$^\circ$ (panels (a)–(c), respectively). Results for both H$_2$ and D$_2$ are presented. For $\theta_n = 0^\circ$ and 90$^\circ$, our results are almost identical to those obtained in [18, 19], where the origin of the different structures observed in the spectra was explained in detail. Briefly, the large peak at low KER corresponds to direct ionization (the mechanism illustrated in figure 7(a)), while all the structures observed above 1 eV are due to the autoionizing decay of the Q$_1$ doubly excited states (the mechanism illustrated in figure 7(b)). At 90$^\circ$, figure 8(c) shows no significant structure.
beyond a KER of 1 eV, which means that the Q₁ doubly excited states of \(^1\Sigma_u^+\) symmetry play a minor role in the photoionization process. Their small contribution to the cross section is more clearly seen in the inset of figure 8(c). In contrast, contribution of the Q₁ \(^1\Sigma_u^+\) states is very important, as can be seen in the KER spectrum at 0° where only states of \(^1\Sigma_u^+\) symmetry can be populated (see figure 8(a)). As discussed in [18, 19], at 0° the peak at a KER of about 1.5 eV is due to the interference between direct ionization and autoionization, while the broad structure above 2 eV is almost entirely due to autoionization. The KER spectrum at 54.7° is very similar to that at 0° because, although Q₁ states of both \(^1\Sigma_u^+\) and \(^1\Pi_u\) symmetries can now be populated, those of \(^1\Pi_u\) symmetry barely contribute to the spectrum (see 8(c)). For the \(D_2\) molecule, the same structures are observed, although they are less pronounced and are shifted 1 eV downward in energy (see [19] for more details).

We focus now on the electron angular distributions. In contrast with the results at a photon energy of 20 eV, the \(F_{LMN}^0\) coefficients exhibit a more complex dependence on the polar angle and energy of the ejected electron than that described in the previous section. This is mainly due to the presence of the Q₁ \(^1\Sigma_u^+\) doubly excited states. These coefficients lead to the angular distributions given in figure 9 for the three orientations discussed above. For the sake of clarity, panel (d) indicates with arrows the selected electron energies in the corresponding KER spectra. For \(\theta_n = 0^\circ\), where only Q₁ states of \(^1\Sigma_u^+\) symmetry are populated, the electron angular distributions exhibit a simple p-like pattern for all final electron energies. These patterns are very similar to those obtained at a photon energy of 20 eV (see figure 5). In other words, autoionization from the Q₁ \(^1\Sigma_u^+\) states still leads to electron emission along the polarization direction independently of the electron energy and independently of how important electron correlation is in these states. Therefore, the main role of the Q₁ \(^1\Sigma_u^+\) states is just to increase the cross section in the regions of the KER spectrum in which direct ionization does not contribute.

For \(\theta_n = 90^\circ\), the angular distribution also exhibits a p-like pattern except in the regions of the KER spectrum where the Q₁ \(^1\Pi_u\) doubly excited states contribute (electron energies between...
Figure 9. Electron angular distribution of H₂ as a function of electron energy for the three following orientations of the polarization vector with respect to the molecular axis: (a) $\theta_n = 0^\circ$, (b) $\theta_n = 54.7^\circ$ and (c) $\theta_n = 90^\circ$. For the sake of clarity, in all angular distributions the maximum has been normalized to unity. Panel (d) shows the cross sections integrated over electron emission angle for the same orientations of the polarization vector: (d.1) $\theta_n = 0^\circ$, (d.2) $\theta_n = 54.7^\circ$ and (d.3) $\theta_n = 90^\circ$. Arrows indicate the electron energies at which the angular distributions are plotted. All results obtained are at $\hbar \omega = 27$ eV.
0 and 3 eV). However, since the absolute value of the cross section in the latter region is very small, the complex angular pattern resulting from the autoionization of these states will be very difficult to observe. The reason for this angular behaviour at low electron energy (i.e. high proton kinetic energy) can be understood by looking at the contributions of the different partial waves. At an electron energy of \(\sim 0.2\) eV (proton energy \(\sim 4.4\) eV), the angular distribution is mainly due to a term containing the \(P_{1/2}(\cos \theta_e)\) Legendre polynomial, which reflects the importance of the \(p_{\pi_u}\) partial wave. As the electron energy increases, e.g. at \(\sim 2.8\) eV (proton energy \(\sim 3.0\) eV), the contribution of the \(p_{\pi_u}\) partial wave increases. In the [3.9, 4.9] eV electron energy range ([2.0, 2.5] eV proton energy range), contribution of the \(p_{\pi_u}\) and \(f_{\pi_u}\) partial waves is comparable, leading to a strong interference that is clearly seen in the angular distribution. At higher electron energies (lower proton energies), the electron distribution is completely characterized by the \(p_{\pi_u}\) contribution, and the ejected electron follows the direction of the polarization vector.

We consider now the case of \(\theta_n = 54.7^\circ\). At this angle, the observed patterns result from the coherent superposition of the amplitudes that lead to the angular distributions at \(\theta_n = 0^\circ\) and \(90^\circ\). For electron energies smaller than 6 eV (proton energies greater than 1.5 eV), the electron is mainly ejected along the molecular axis and not along the direction of the polarization vector (in contrast with the results at 20 eV, see figure 5). This is a consequence of the small contribution of \(^1\Pi_u\) symmetry: as ionization is dominated by \(^1\Sigma_u^+\) symmetry, the electron tends to follow the molecular axis. At an electron energy of \(\sim 6.6\) eV the situation changes drastically; the electron is ejected perpendicular to the polarization vector, since the contribution of the \(Q_{1/1^+}^\text{ }^1\Sigma_u^+\) states has a minimum at this energy (see figure 5(a)) and interference with the \(\Pi_u\) amplitude is largest. As discussed above, the minimum in the \(^1\Sigma_u^+\) amplitude is due to the interference between the resonant and nonresonant ionization processes. Therefore, the unusual behaviour observed at an electron energy of 6.6 eV is a consequence of this interference. As the electron energy increases, the nonresonant process dominates and the usual behaviour is restored, i.e. the electron is ejected following the polarization direction and the distribution has an almost p-like pattern.

The results obtained for D\(_2\) (not shown) are very similar to those obtained for H\(_2\), with the only exception of \(\theta_n = 54.7^\circ\) and an electron energy of \(\sim 8\) eV (deuteron energy of \(\sim 0.5\) eV). At this electron energy, the KER at \(0^\circ\) presents a minimum and, consequently, we should expect that the angular distribution does not follow the molecular axis, which is indeed the case. However, as we have seen above, in H\(_2\), the angular distribution is perpendicular to the polarization direction, but in D\(_2\) it is perpendicular to the molecular axis. This is because, at this electron energy, the \(^1\Pi_u\) contribution is largely dominant and, consequently, the angular distribution is perpendicular to the molecular axis.

Figure 10 shows the H\(_2\) angular distributions integrated over the whole electron energy range. They are very similar to those obtained at a photon energy of 20 eV (see figure 5), which means that any contribution from autoionization is completely diluted. The corresponding D\(_2\) angular distributions (not shown) are almost indistinguishable from those of H\(_2\).

We now consider the electron angular distribution that is obtained from a set of randomly oriented molecules. This distribution is entirely determined by the electron beta parameter defined in (12). The calculated beta parameter is presented in the left panel of figure 11 as a function of the electron kinetic energy for both H\(_2\) and D\(_2\). The figure also shows the electron angular distribution for selected electron energies (symbols \(A\), \(B\) and \(C\)). The beta parameter is close to 2 for electron energies larger than 8 eV and is richly structured in the region where
autoionization from the $Q_1$ doubly excited states is dominant. For an electron energy of 6.6 eV (see figure 8), there is a deep minimum for both $H_2$ and $D_2$, which is related to the interference discussed above. The only experimental result for the electron beta parameter at this photon energy (26.9 eV) was reported by Hikosaka and Eland [54]. They measured the electron beta parameter associated with the angular distribution integrated over electron energy and found a value of $\beta_e \approx 1.7 \pm 0.05$. From our calculations, the ‘integrated’ electron beta parameter for $H_2$ ($D_2$) for electrons associated with the dissociative process takes a value of 0.23 (0.16), whereas the beta parameter for electrons associated with the nondissociative process (i.e. associated with the production of bound vibrational states of the $H_2^+(\nu)$ ion) takes a value of 1.90 (1.90). The ‘integrated’ total beta parameter, which includes the contribution from the dissociative and nondissociative processes, takes a value of 1.85 (1.88), which is very close to the experimental result of Hikosaka and Eland [54]. This value is close to that obtained at a photon energy of 20 eV because nondissociative ionization is largely dominant and the contribution from autoionization to this process is very small.

The ionic asymmetry parameter is shown in the right panel of figure 11 as a function of the proton kinetic energy for both $H_2$ and $D_2$. The figure also shows the proton angular distribution for a few selected proton energies (symbols $A$, $B$ and $C$). Note that, at variance with the results at 20 eV, sometimes the protons do not follow the polarization direction (see e.g. the result labelled $C$ in the figure). For proton energies larger than 2 eV, the nuclear beta parameter is close to 2 for both molecules. This is because, in this proton energy range, the contribution from the $^1\Pi_u$ symmetry is negligible compared with that of the $^1\Sigma_u^+$ one. At smaller proton energies, the interference between the resonant and nonresonant process (see also figure 8) leads to a minimum at 1.1 and 0.4 eV for $H_2$ and $D_2$, respectively. At these electron energies the dominant process changes from a pure $^1\Sigma_u^+ \rightarrow ^1\Sigma_u^+$ transition to a mixture of $^1\Sigma_u^+ \rightarrow ^1\Sigma_u^-$ and $^1\Sigma_u^+ \rightarrow ^1\Pi_0$ transitions for $H_2$, and to a pure $^1\Sigma_u^+ \rightarrow ^1\Pi_0$ transition for $D_2$ (that is why in the latter case $\beta_{D^+} \approx -1$). Hikosaka and Eland [54] measured the integrated ionic asymmetry
Figure 11. Left panel, electron asymmetry parameter as a function of electron energy. Right panel, proton asymmetry parameter as a function of proton energy. In both figures, the results for H$_2$ and D$_2$ are shown by full black and dashed red lines, respectively. The lobes represent the electron/proton angular distributions at the electron/proton energies labelled by the symbols A, B and C. The nonresonant results are also displayed in both panels for both molecules. All results are obtained at $\hbar\omega = 27$ eV.

parameter for the H$_2$ molecule, $\beta_{H^+} \approx 0.16 \pm 0.09$. We have found 0.26 for H$_2$ and 0.63 for D$_2$. These values are slightly larger than those obtained at 20 eV (0.073 for H$_2$ and 0.068 for D$_2$) due to the contribution of the doubly excited states.

4.3. $\hbar\omega = 33$: the role of the Q$_2$ resonant states

At this photon energy, not only the Q$_1$ but also the Q$_2$ doubly excited states are accessible. Energy positions and autoionization widths for the Q$_2$ states of $^1\Sigma^+_u$ and $^1\Pi_u$ symmetry have been obtained in previous theoretical work (see e.g. [40], [56]–[59] and references therein). The resonance parameters resulting from the Q$_2$ wave functions calculated in the present work are in very good agreement with those of Tennyson [57], Sánchez and Martín [40] and Jonsell et al [58]. The agreement is also good with the energy positions calculated by Vanne et al [59] in the range of internuclear distances 0–6 au, but the latter are more accurate at much larger internuclear distances. Nevertheless, inaccuracies in the calculated wave functions beyond $R = 6$ au will have a negligible effect in the calculated ionization cross sections because the doubly excited states that are dominantly populated autoionize at shorter internuclear distances.

At a photon energy of 33 eV, ionization can lead to H$_2^+$ not only in the ground electronic state $^2\Sigma^+_g(1s\sigma_g)$ but also in the excited electronic state $^2\Sigma^+_u(2p\sigma_u)$. In the case of dissociative photoionization, the competing processes are

$$H_2(X^1\Sigma^+_g) + \hbar\omega \rightarrow H_2^+(1s\sigma_g) + e^- \rightarrow H^+ + H(1s) + e^- \quad (39)$$

$$\rightarrow H_2(Q_1) \rightarrow H_2^+(1s\sigma_g) + e^- \rightarrow H^+ + H(1s) + e^- \quad (40)$$
and

\[ H_2(X^1\Sigma_g^+) + \hbar \omega \rightarrow H_2^+(2p\sigma_u) + e^- \rightarrow H^+ + H(1s) + e^- \]  \hspace{1cm} (41)

\[ \rightarrow H_2(Q_2) \rightarrow H_2^+(1s\sigma_g) + e^- \rightarrow H^+ + H(1s) + e^- \]  \hspace{1cm} (42)

\[ \rightarrow H_2(Q_2) \rightarrow H_2^+(2p\sigma_u) + e^- \rightarrow H^+ + H(n = 2) + e^- . \] \hspace{1cm} (43)

All these processes are schematically represented in figure 12. The energy difference between the lowest two ionization thresholds, i.e. between the lowest two states of H$_2^+$, \$2\Sigma_g^+(1s\sigma_g)$ and \$2\Sigma_u^+(2p\sigma_u)$, is about 17 eV in the FC region of H$_2$. If H$_2$ is directly ionized in a vertical transition from the ground state, the photoelectron will have an energy of about \$E_e = h\omega - 16\ \text{eV}\$ when the remaining H$_2^+$ is left in the 1s\sigma_g state, whereas it will have \$E_e = h\omega - 33\ \text{eV}\$ when it is left in the repulsive 2p\sigma_u state. Both ionization paths are distinguishable by the energy (figures 12(a) and (b)). The photoelectron energies associated with autoionization also depend on the final H$_2$ state. Since autoionization can occur at internuclear distances \$R\$ much larger than the equilibrium distance (i.e. outside the FC region), the energy of the autoionized electron in the 1s\sigma_g and 2p\sigma_u channels can be more similar than in the direct ionization process. In fact, the larger the internuclear distance at which autoionization from the Q$_2$ state occurs, the closer the photoelectron energy associated with the \$2\Sigma_g^+(1s\sigma_g)\$ and \$2\Sigma_u^+(2p\sigma_u)\$ channels (see figure 12(d)). Also, the energy of the electron resulting from autoionization of the Q$_1$ state, which can only decay to the \$2\Sigma_g^+(1s\sigma_g)\$ channel, can be more similar to that of an electron directly ionized into the \$2\Sigma_u^+(2p\sigma_u)\$ channel. As we will see below, although this semiclassical image is useful to qualitatively assign regions of the KER spectrum to the different ionization processes, one has to be very careful in using it when quantum nuclear effects cannot be neglected.

In figure 13, we present the KER spectrum resulting from integration of the fully differential cross sections over the electron emission angle. The results are shown again for the three molecular orientations considered in the previous sections. Contributions from the two ionization thresholds, \$2\Sigma_g^+(1s\sigma_g)\$ and \$2\Sigma_u^+(2p\sigma_u)\$, are shown separately. For \$\theta_n = 90^\circ\$, the present KER spectra are almost identical to those obtained in [21, 22].

At \$\theta_n = 0^\circ\$, the KER spectrum associated with the \$2\Sigma_g^+(1s\sigma_g)\$ threshold is very similar to that obtained at 27 eV, except for the fact that the region in which autoionization is dominant extends up to proton energies of 7.5 eV. Again, the proton energy region corresponding to direct ionization restricts to the interval between 0 and 1 eV. The KER spectrum associated with the \$2\Sigma_u^+(2p\sigma_u)\$ threshold is only visible at the higher proton energies and results almost entirely from direct ionization. Almost no autoionization from the Q$_2$ \$1\Sigma_u^+\$ states is observed because these states are barely populated by a photon of 33 eV (see figure 1) and their autoionization widths are significantly smaller than those of the Q$_1$ \$1\Pi_u^+\$ states. At \$\theta_n = 90^\circ\$, the situation is different. In this case, there is almost no trace of autoionization coming from the Q$_1$ \$1\Pi_u^+\$ states (exactly as for a photon energy of 27 eV). Apart from the large peak at proton energies below 1 eV, which is due to direct ionization through the \$2\Sigma_g^+(1s\sigma_g)\$ threshold, all the other structures seen in the spectrum are due to autoionization of the Q$_2$ \$1\Pi_u\$ states through either the \$2\Sigma_g^+(1s\sigma_g)\$ or the \$2\Sigma_u^+(2p\sigma_u)\$ threshold. A detailed explanation of the origin of the different peaks observed in this spectrum can be found in [17, 21, 22]. At \$\theta_n = 54.7^\circ\$, we find again a combination of the effects seen at \$0^\circ\$ and \$90^\circ\$. This analysis is valid for both H$_2$ and D$_2$.

As mentioned above, an important point is that ionization is effectively possible through the \$2\Sigma_g^+(1s\sigma_g)\$ and \$2\Sigma_u^+(2p\sigma_u)\$ ionization thresholds in a wide range of proton (viz electron) energies.
Figure 12. Semiclassical pathways for dissociative ionization of H$_2$ by a 33 eV photon. (a) Direct dissociative ionization leading to H$_2^+$ (1$s\sigma_g$) (equation (39) in the text). (b) Direct dissociative ionization leading to H$_2^+$ (2$p\sigma_u$) (equation (41) in the text). (c) Resonant dissociative ionization through the lowest Q$_1$ doubly excited states leading to H$_2^+$ (1$s\sigma_g$) (equation (40) in the text). (d) Resonant dissociative ionization through the lowest Q$_2$ doubly excited states leading to either H$_2^+$ (1$s\sigma_g$) (equation (42) in the text) or H$_2^+$ (2$p\sigma_u$) (equation (43) in the text). Symbols and notations are as in figure 7.

(4–7.5 eV in the 0° case and 3–7 eV in the 90° case). Since these thresholds are degenerate at R = ∞, it is very important to account for the proper asymptotic conditions discussed in section 3.2 in order to compare with the experimental results in which the proton ejection direction is determined. Accounting for the proper boundary conditions is practically irrelevant when ionization proceeds exclusively through the $^2\Sigma_g^+$ (1$s\sigma_g$) threshold because contribution
Figure 13. Cross sections integrated over electron emission angle as functions of electron (proton) energy for H$_2$ (black line) and D$_2$ (red dashed line), and the three orientations of the molecule with respect to the polarization direction: (a) $\theta_n = 0^\circ$, (b) $\theta_n = 54.7^\circ$ and (c) $\theta_n = 90^\circ$. All results are obtained at $\hbar \omega = 33$ eV.

from the second term in equation (33) to the cross section is zero. This is essentially the case for the two photon energies investigated in the previous sections. However, in the present case, both terms contribute and, consequently, the angular distribution will be significantly different from that obtained from either the $^2 \Sigma_g^+$($1s\sigma_g$) or the $^2 \Sigma_u^+$(2p$\sigma_u$) channel.

Figures 14 and 15 show, respectively, the H$_2$ and D$_2$ electron angular distributions for the usual three molecular orientations and for specific energies of the ejected electron. These electron energies are indicated by arrows in the lower panel of the figures. When the molecule is parallel to the polarization direction, we see the typical p-like pattern observed at lower photon energies but only for electron energies larger than 7 eV (proton energies smaller than 4 eV). At smaller electron energies, the size of the two lobes is no longer the same and their relative magnitude oscillates from one side of the molecule to the other as the electron energy decreases. When the molecule is perpendicular to the polarization direction (the case investigated in [7]), the angular distributions are found to vary strongly with electron energy. At electron energies below 1 eV, i.e. in the region where direct ionization is the dominant process, the angular distribution exhibits the typical p-pattern perpendicular to the molecular axis. As soon as one enters the region of electron energies in which autoionization is the dominant process (i.e. as electron energy decreases), the angular distribution changes to a sort of butterfly shape, then develops additional lobes and ends up in a four-lobed pattern similar to a d-distribution. Furthermore, as in the parallel case, there is a strong upward–downward asymmetry, in particular in a narrow range of electron energies $E_e \simeq 5–7$ eV corresponding to proton kinetic energies of $\simeq 8–10$ eV. It is important to note that, for both parallel and perpendicular orientations, the asymmetry is more pronounced in the region of electron energies in which ionization through the $^2 \Sigma_g^+$(1s$\sigma_g$) and $^2 \Sigma_u^+$(2p$\sigma_u$) channels overlap. Such an asymmetry cannot be observed at 20 and 27 eV because dissociative photoionization proceeds almost exclusively through the first ionization threshold. At those photon energies, the electron angular distributions are totally symmetric with respect to the inversion centre of the molecule (see for example figures 4, 5 and 9).

New Journal of Physics 11 (2009) 043020 (http://www.njp.org/)
Figure 14. Electron angular distribution of H₂ as a function of electron energy for the three orientations of the polarization vector with respect to the molecular axis: (a) $\theta_n = 0^\circ$, (b) $\theta_n = 54.7^\circ$ and (c) $\theta_n = 90^\circ$. For the sake of clarity, in all angular distributions the maximum has been normalized to unity. Panel (d) shows the cross sections integrated over electron emission angle for the same three molecular orientations: (d.1) $\theta_n = 0^\circ$, (d.2) $\theta_n = 54.7^\circ$ and (d.3) $\theta_n = 90^\circ$. The arrows indicate the electron energies at which the angular distributions are plotted. All results are obtained at $\hbar \omega = 33$ eV.

In [7], the origin of the asymmetry at $90^\circ$ was analysed by comparing with model calculations in which only the direct ionization channels, $^2\Sigma_g^+ (1s\sigma_g)$ and $^2\Sigma_u^+ (2p\sigma_u)$, and the lowest Q₂ state of $\Pi_u$ symmetry were included. The model angular distributions are very similar to those obtained from the full calculation, showing that the Q₁ states are not responsible for its occurrence. Furthermore, exclusion of the two direct-ionization channels also led to asymmetric angular distribution. Consequently, the origin of the asymmetry in this particular case is the interference between the $1s\sigma_g$ and $2p\sigma_u$ channels resulting from autoionization of the Q₂ states.
Therefore, it is only the coherent superposition of these pathways that allows for a localization of the bound electron in the dissociating H$_2^+$. At 0°, the situation is different because, in this case, the Q$_1$ $^1\Sigma_u^+$ states autoionize quite efficiently and almost no contribution is obtained from the corresponding Q$_2$ states. The asymmetry results now from the interference between direct ionization through the $^2\Sigma_u^+$ (2p$_\sigma$u) channel and autoionization from the Q$_1$ $^1\Sigma_u^+$ states through the $^2\Sigma_u^+$ (1s$_\sigma$g) channel. In any case, the asymmetry is again the result of the interference between 1s$_\sigma$g and 2p$_\sigma$u ionization channels.

Our theoretical predictions at 90° have been recently confirmed by COLTRIMS experiments [7]. A detailed comparison between theory and experiment can be found in that reference. Our theoretical results are also consistent with those reported in a previous experiment [4] by averaging over KER intervals of 2.5–3 eV. In the latter experiment, evidence of asymmetric angular distributions was also obtained at 0°, in agreement with the present theoretical results.

Figure 15. Same as in figure 14 but for D$_2$. 

New Journal of Physics 11 (2009) 043020 (http://www.njp.org/)
The calculated angular distributions at 54.7° are more complex than at 0° and 90°. Furthermore, they are not just a linear combination of the angular distributions at 0° and 90° because coherence between the $^1\Sigma_u^+$ and $^1\Pi_u$ amplitudes is large. Therefore, they reflect the interference between all the ionization channels described at the beginning of this subsection (see the set of equations following equation (39)). For this orientation, comparison with the experimental results of [4] is difficult due to the limited energy resolution of the experiment and the large variation of the angular distributions with electron energy. Thus, further experimental work is needed in order to confirm the predicted coherence between $^1\Sigma_u^+$ and $^1\Pi_u$ molecular states at 54.7°.

Figure 16 shows the electron angular distribution for the H$_2$ molecule integrated over the whole electron energy range for the three molecular orientations. In the parallel case, where only the Q$_1$ $^1\Sigma_u^+$ resonant states contribute significantly, the observed pattern is similar to those obtained at 20 and 27 eV. For the ‘magic angle’, the electron is emitted in the direction of the polarization vector but the contribution of the Q$_2$ $^1\Pi_u$ states produces additional lobes perpendicular to the polarization direction. In the perpendicular case, the observed pattern is completely different from those displayed in figures 5 and 10 and is exclusively due to the Q$_2$ $^1\Pi_u$ states. The results for D$_2$ (not shown) are similar to those obtained for H$_2$. It can be seen that, in all cases, the angular distributions are completely symmetric with respect to the proton emission direction. This is because, after integration over the electron energy, the coherence between the 1s$\sigma_g$ and 2p$\sigma_u$ ionization channels is lost. This coherence is only possible when the electron has exactly the same energy in both channels and this can only be known by measuring the energy of the ejected electron. Since the asymmetry oscillates as a function of electron energy (see figures 14 and 15), integration over this energy leads to the compensation of the various asymmetry patterns.

It is interesting to emphasize here that, as explained in detail in [7], the observed asymmetry cannot be predicted by using semiclassical arguments (as those used in figures 12(a)–(d) for pedagogical purposes). In this simple model, the system always strictly follows the potential
energy curves and only vertical transitions between them are allowed. These vertical transitions may occur as a result of photon absorption (vertical lines on the left) or autoionization decay (vertical lines on the right). In this framework, all molecules have an identically well-defined value of the internuclear distance during the transition and, consequently, any possible direct energy exchange between electronic and nuclear motions is neglected. For example, in such a model the electron energy resulting from the path shown in figure 12(d), corresponding to resonant photoionization through the $2p\sigma_u$ channel, would be equal to the energy difference between the Q$_2$ and the $2p\sigma_u$ curve at the marked internuclear distance. A similar reasoning predicts the electron energy along the path corresponding to resonant photoionization through the $1s\sigma_g$ channel. The model predicts that the maximum possible value of the KER in the $1s\sigma_g$ channel is 8.1 eV (corresponding to autoionization decay at infinite internuclear distance), which is the minimum possible value of the KER in the $2p\sigma_u$ channel (corresponding also to autoionization decay at infinite internuclear distance). Therefore, no interference between the $1s\sigma_g$ and $2p\sigma_u$ channels can occur within this model at 90$^\circ$ because the electron energies and the KER regions for transitions to $1s\sigma_g$ and $2p\sigma_u$ channels from the Q$_2$ doubly excited state would have no overlap, and hence the electron ejection would always be symmetric. Our fully quantum mechanical treatment shows that autoionizing transitions to the $1s\sigma_g$ state can occur beyond 8.1 eV and that autoionizing transitions to the $2p\sigma_u$ state are possible even at zero KER (see figure 13(c) and bottom of figures 14(d.3) and 15(d.3)). Thus the angular distribution can exhibit an asymmetry over the whole region of KER. Quantum mechanical effects are also responsible for the overlap between the $1s\sigma_g$ and $2p\sigma_u$ channels in the KER spectrum at 0$^\circ$ (see figure 13(a) and bottom of figures 14(d.1) and 15(d.1)). Strictly speaking, a symmetric dissociation in the presence of resonances is the exception rather than the rule. It becomes quantitatively significant in the region where both channels are comparably active; however, it is also visible in regions where one of the channels dominates (panels (b)–(f) of figure 12).

Also it is worth noting that the observed asymmetry has no relation to the direction in which the charged fragment is emitted: sometimes the larger lobes are found on the proton side, sometimes on the hydrogen side. Between consecutive oscillations, there are KER values for which the distribution is practically symmetric. Thus, the asymmetry cannot be explained by a preferred attractive interaction between the proton and the escaping electron (the latter is too fast to be efficiently perturbed by the slow proton, except possibly in the region of the maximum allowed KER).

To complete this section we study the proton angular distribution and the electron distribution for randomly distributed molecules. In figure 17, we present the H$_2$ and D$_2$ photoelectron beta parameter corresponding to the angular distributions in the $^2\Sigma_g^+(1s\sigma_g)$ and $^2\Sigma_u^+(2p\sigma_u)$ ionization channels, and to the total angular distribution. For electron energies larger than 6 eV, the ‘total’ electron beta parameter is almost identical to the beta parameter associated with the $^2\Sigma_g^+(1s\sigma_g)$ channel. This parameter strongly oscillates in this region, which is mainly due to the interference between autoionization from the Q$_1$ $^1\Sigma_u^+$ and Q$_2$ $^1\Pi_u$ states and direct ionization. For energies $\leq$ 6 eV, the ‘total’ electron beta parameter is very similar to the beta parameter associated with the $^2\Sigma_u^+(2p\sigma_u)$ channel. In this region, the beta parameter varies smoothly with electron energy because only the Q$_2$ $^1\Pi_u$ states autoionize significantly in this energy range. The results for the D$_2$ molecule are similar to those obtained for H$_2$, but in this case the different structures are shifted $\sim$ 1 eV (a similar shift was observed in the cross sections integrated over electron emission angle, see figure 13). In table 1, we present the electron beta parameters associated with the angular distributions obtained after
integration over electron energy in the nondissociative and dissociative regions, as well as over the whole range of electron energy. At this photon energy, the photoelectron beta parameter has been measured [4]. They reported the values $\beta_e \approx 1.0 \pm 0.1$ in the electron energy range $[0, 5.0]$ eV, and $\beta_e \approx 0.15 \pm 0.1$ in the electron energy range $[5, 10.0]$ eV. Integrating our angular distributions in the same electron energy ranges, we obtain values of $\beta_e = 1.16$ and 0.20, respectively, which agree reasonably well with the experimental values.

The ionic asymmetry parameters for $H_2$ and $D_2$ are shown in the right panel of figure 17. These parameters strongly depend on proton or deuteron energy, which is a consequence of the different contributions of the various doubly excited states to the different ionization thresholds. Integrating over proton or deuteron energy the angular distributions associated with the first ionization threshold ($1s \sigma_g$), we obtain a beta parameter equal to 0.20 for $H_2$ and 0.15 for $D_2$, which means that $\Sigma_u$ and $\Pi_u$ contributions are comparable in magnitude (see (11)). For the $2p\sigma_u$ ionization threshold, the ‘integrated’ ionic asymmetry parameter takes a value of $-0.44$ for $H_2$ and $-0.58$ for $D_2$. When contribution from the different ionization thresholds is not resolved, the ionic asymmetry parameter takes a value of 0.03 for $H_2$ and $-0.11$ for $D_2$. Lafosse et al [4] measured the proton beta parameter in two proton energy ranges: $[2.5, 5.0]$ eV with a value of $\beta_{pH} \approx -0.1 \pm 0.1$ and $[4.5, 9.0]$ eV with a value of $\beta_{pH} \approx 0.25 \pm 0.1$. Integrating the

**Table 1.** Photoelectron beta parameter for $H_2$ and $D_2$ at $\hbar \omega = 33$ eV. $\beta_e^N$, beta parameter for the nondissociative process; $\beta_e^D$, beta parameter for the dissociative process; $\beta_e^T$, total beta parameter.

|          | $H_2$       | $D_2$       |
|----------|-------------|-------------|
| $1s\sigma_g$ | $2p\sigma_u$ | $1s\sigma_g$ | $2p\sigma_u$ |
| $\beta_e^N$ | $\beta_e^D$ | $\beta_e^T$ | $\beta_e^T$ |
| 1.92      | 0.56        | 1.83        | 0.83         |
| 1.92      | 0.52        | 1.88        | 0.87         |

**Figure 17.** Left panel, electron asymmetry parameter as a function of electron energy for $H_2$ (upper panel) and $D_2$ (lower panel). The contribution from the first two ionization thresholds is also included: blue dashed line, $1s\sigma_g$ contribution; red dot-dashed line, $2p\sigma_u$ contribution. Right panel, ionic asymmetry parameter as a function of the proton energy for $H_2$ (full lines) and for $D_2$ (dashed lines). The contribution from the first two ionization thresholds is also included: blue line, $1s\sigma_g$ contribution; red line, $2p\sigma_u$ contribution. All results obtained at $\hbar \omega = 33$ eV.
theoretical angular distributions, we obtain a value of $\beta_{\text{H}^+} \approx -0.32$ in the proton energy range [2.5, 5.0] eV and a value equal to $\beta_{\text{H}^+} \approx 0.15$ in the proton energy range [4.5, 7.35] eV (note that the maximum proton energy at a photon energy of 33 eV is 7.35 eV), which agree reasonably well with the experimental results.

5. Conclusions

We have studied the MFPADs of H$_2$ and D$_2$ in dissociative photoionization produced by linearly polarized light. The theoretical method includes the coupling between the different ionization and autoionization channels, and accounts for electron correlation as well as nuclear motion of the parent molecule and residual molecular ion. The coupling between ionization and dissociation channels due to the delayed autoionization of the molecular doubly excited states is also included. We have evaluated fully differential photoelectron angular distributions as well as proton and electron beta parameters of H$_2$ and D$_2$ at three different photon energies: 20, 27 and 33 eV. At 20 eV, the angular distributions barely depend on electron energy and exhibit a simple p-wave pattern. This is the result of a direct ionization process that leads to dissociation of the remaining H$_2^+$ or D$_2^+$ ions through the $X^2\Sigma_g^+(1s\sigma_g)$ state. At 27 eV, the Q$_1$ doubly excited states are populated and, consequently, the ensuing autoionization process is expected to affect the angular distributions. We show, however, that, at this photon energy, the calculated angular distributions are very similar to those obtained at 20 eV, except when the molecule is oriented perpendicularly to the polarization direction and the electron energy is relatively small. This is due to autoionization of the Q$_1$ $^1\Pi_u$ doubly excited states through the $X^2\Sigma_g^+(1s\sigma_g)$ channel. Nevertheless, the contribution of this process to the total dissociative ionization cross section is very small. At 33 eV, the situation is much more interesting because the Q$_2$ doubly excited states, which can be populated at this photon energy, can also decay to the $^2\Sigma_u^+(2p\sigma_u)$ state. We have shown that the delayed ionization from the Q$_1$ and Q$_2$ doubly excited states is responsible for a strong asymmetry in the electron angular distributions along the molecular axis which, in addition, changes rapidly with the energy of the ejected electron. This interesting effect is observed for molecules oriented either parallel or perpendicular to the polarization direction and is a consequence of the interference between the $X^2\Sigma_g^+(1s\sigma_g)$ and $^2\Sigma_u^+(2p\sigma_u)$ ionization channels that is possible because the energy of the ionized electron can be the same in both channels. The effect can only be observed in experiments in which the direction of H$^+$ or D$^+$ emission is unambiguously determined as e.g. in COLTRIMS experiments reported recently [7]. This should be a general phenomenon in all diatomic homonuclear molecules whenever photoionization leads to electrons with the same energy in two channels of different parity. In the present problem, the appropriate conditions are provided by the delayed ionization from the H$_2$ or D$_2$ doubly excited states. But there are other systems, e.g. in k-shell photoionization of N$_2$, in which g and u ionization channels are nearly degenerate and, consequently, the appropriate conditions for efficient g–u interferences are automatically fulfilled [8, 9].

Our theoretical study has been completed by the analysis of the electronic and nuclear asymmetry (beta) parameters at the same photon energies. Although the corresponding angular distributions do not exhibit any reminiscence of the above asymmetry, the beta parameters strongly vary in the regions of electron or ion energies in which autoionization is the dominant process. The calculated values of these parameters are in good agreement with the existing experimental values.
Acknowledgments

We are grateful to Reinhard Dörner and Danielle Dowek for many illuminating discussions on the origin of the asymmetry and for providing us with all the details concerning their measurements. This work was partially supported by the Spanish Ministerio de Ciencia e Innovación (contract no. FIS2007-60064) and the European Science Foundation (COST action CM0702). Calculations were performed at the Barcelona Supercomputer Center Mare Nostrum and the Centro de Computación Científica UAM.

References

[1] Lawrence E O and Chaffe M A 1930 Phys. Rev. 36 1099–100
[2] Ullrich J, Moshammer R, Dörner R, Jagutzki O, Mergel V, Schmidt-Böcking H and Spielberger L 1997 J. Phys. B: At. Mol. Opt. Phys. 30 2917–74
[3] Jahnke T et al 2002 Phys. Rev. Lett. 88 073002
[4] Lafosse A, Lebech M, Brenot J C, Guyon P M, Spielberger L, Jagutzki O, Houver J C and Dowek D 2003 J. Phys. B: At. Mol. Opt. Phys. 36 4683–702
[5] Jahnke T et al 2004 Phys. Rev. Lett. 93 083002
[6] Ullrich J, Moshammer R, Dorn A, Dörner R, Schmidt L Ph H and Schmidt-Böcking H 2003 Rep. Prog. Phys. 66 1463–545
[7] Martin F et al 2007 Science 315 629–33
[8] Schöffler M S et al 2008 Science 320 920–3
[9] Zimmermann B et al 2008 Nat. Phys. 4 640–55
[10] Weber T et al 2004 Nature 431 437
[11] Weber Th et al 2004 Phys. Rev. Lett. 92 163001
[12] Gisselbrecht M et al 2006 Phys. Rev. Lett. 96 153002
[13] Akoury D et al 2007 Science 318 949
[14] Kreidi K et al 2008 Phys. Rev. Lett. 100 133005
[15] Reddish T J, Colgan J, Bolognesi P, Avaldi L, Gisselbrecht M, Lavollée M, Pindzola M S and Huetz A 2008 Phys. Rev. Lett. 100 153001
[16] Latimer C J, Geddes J, MacDonald M A, Kouchi N and Dunn K F 1996 J. Phys. B: At. Mol. Opt. Phys. 29 6113–21
[17] Ito K, Hall R I and Ukai M 1996 J. Chem. Phys. 104 8449–57
[18] Sánchez I and Martín F 1997 Phys. Rev. Lett. 79 1654–7
[19] Sánchez I and Martín F 1998 Phys. Rev. A 57 1006–17
[20] Martín F 1999 J. Phys. B: At. Mol. Opt. Phys. 32 R197–231
[21] Sánchez I and Martín F 1999 Phys. Rev. Lett. 82 3775–8
[22] Sánchez I and Martín F 1999 Phys. Rev. A 60 2200–6
[23] Aoto T, Hikosaka Y, Hall R I, Ito K, Fernández J and Martin F 2004 Chem. Phys. Lett. 389 145–9
[24] Chesnel J-Y, Martina D, Sobocinski P, Kamalou O, Frémont F, Fernández J and Martin F 2004 Phys. Rev. A 70 010701
[25] Laurent G et al 2006 Phys. Rev. Lett. 96 173201
[26] Fernández J, Fojón O A, Palacios A and Martín F 2007 Interference from fast electron emission in molecular photoionization Phys. Rev. Lett. 98 043005
[27] Fernández J, Fojón O A and Martin F 2009 Phys. Rev. A. 79 023420
[28] Fernández J, Yip F L, Rescigno T N, McCurdy C W and Martin F 2009 Phys. Rev. A at press
[29] Semenov S K and Cherepkov N A 2003 J. Phys. B: At. Mol. Opt. Phys. 36 1409–22
[30] Dill D 1976 J. Chem. Phys. 65 1130–3

New Journal of Physics 11 (2009) 043020 (http://www.njp.org/)
[31] Lafosse A, Lebech M, Brenot J C, Guyon P M, Jagutzki O, Spielberger L, Vervloet M, Houwer J C and Dowek D 2000 Phys. Rev. Lett. 84 5987–90
[32] Wallace S and Dill D 1978 Phys. Rev. B 17 1692–9
[33] Tully J C, Berry R S and Dalton B J 1968 Phys. Rev. 176 95–105
[34] Cacelli I, Carravetta V, Rizzo A and Moccia R 1991 Phys. Rep. 205 283–351
[35] Sánchez I and Martin F 1997 J. Chem. Phys. 106 7720–30
[36] Bardsley J N 1968 J. Phys. B: At. Mol. Phys. 1 349
[37] Hazi A U, Rescigno T N and Kurilla M 1981 Phys. Rev. A 23 1089
[38] Bachau H, Cormier E, Decleva P, Hansen J E and Martin F 2001 Rep. Prog. Phys. 64 1601–729
[39] Kolos W, Szalewicz K and Monkhurst H J 1986 J. Chem. Phys. 84 3278–83
[40] Sánchez I and Martin F 1999 J. Chem. Phys. 110 6702–13
[41] Fernández J and Martín F 2001 J. Phys. B: At. Mol. Opt. Phys. 34 4141–53
[42] Latimer C J, Dunn K F, Kouchi N, McDonald M A, Srigengan V and Geddes J 1993 J. Phys. B: At. Mol. Opt. Phys. 26 1 595–600
[43] Samson J A R and Cairns R B 1965 J. Opt. Soc. Am. 55 1035–40
[44] Lee L C, Carlson R W and Judge D L 1976 J. Quant. Spectrosc. Radiat. Transfer 16 873–7
[45] Chung Y M, Lee E-M, Masuoka T and Samson J A R 1993 J. Chem. Phys. 99 885–9
[46] Samson J and Haddad G 1994 J. Opt. Soc. Am. B 11 277–9
[47] Latimer C J, Dunn K F, O’Neill F P, MacDonald M A and Kouchi N 1995 J. Chem. Phys. 102 722–5
[48] Dutta C M, Chapman F M Jr and Hayes F 1977 J. Chem. Phys. 67 1904–8
[49] O’Neil S V and Reinhart W P 1978 J. Chem. Phys. 69 2126–42
[50] Cacelli I, Moccia R and Rizzo A 1993 J. Chem. Phys. 98 8742–8
[51] Semenov S K and Cherepkov N A 1998 Chem. Phys. Lett. 291 375–80
[52] Sánchez I and Martin F 1997 J. Chem. Phys. 107 8391–6
[53] Arfken G B and Weber H J 2005 Mathematical Methods For Physicists (New York: Academic)
[54] Hikosaka Y and Weber H J 2003 J. Electron. Spectrosc. Relat. Phenom. 133 77–86
[55] Eland J H D, Takahashi M and Hikosaka Y 2000 Faraday Discuss. 115 119–26
[56] Guberman S L 1983 J. Chem. Phys. 78 1404
[57] Tennyson J 1996 At. Data. Nucl. Data Tables 64 253
[58] Jonssell S, Saenz A, Froelich P, Forrey R C, Côté R and Dalgarno A 2002 Phys. Rev. A 65 042501
[59] Vanne Y V, Saenz A, Dalgarno A, Forrey R C, Froelich P and Jonssell S 2006 Phys. Rev. A 73 062706

New Journal of Physics 11 (2009) 043020 (http://www.njp.org/)