

Single-photon double ionization of the hydrogen molecule

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Abstract

We investigate the single-photon double ionization of molecular hydrogen theoretically over a wide range of photon energies. Our numerical approach is based on the half-collision picture of single-photon multiple ionization and employs a mixed quantum-classical method that splits the double ionization process into a shake-off and a knockout part. We demonstrate that this approach, which has been applied to the double photoionization of helium before, can be successfully extended to the case of molecular target systems with two separate nuclei. The treatment given here allows for both a computationally simple way of calculating molecular double photoionization in reasonable agreement with experiment and recent *ab initio* calculations, and a physical understanding of the results in terms of a simple quasiclassical picture.

1. Introduction

The ionization of an atom or molecule by a single photon is arguably one of the cleanest ways to study the correlated dynamics of N -body Coulomb systems: the perturbation of the target is limited to an infinitely short time span and transfers a precisely controlled amount of energy, while the subsequent evolution of the system is purely governed by the Coulombic forces between the particles. Nevertheless, the quantum-mechanical description of such a process remains a difficult task: time-independent methods [1], where the dipole matrix element $\langle \psi_f | \sum_i z_i | \psi_i \rangle$ corresponding to first-order perturbation theory for the photon–atom or photon–molecule interaction is calculated, usually suffer from the fact that adequate final-state wavefunctions ψ_f taking proper account of interelectronic correlations are not known. Time-dependent methods such as close-coupling calculations [2] or approaches based on complex scaling [3], on the other hand, require a huge numerical effort, especially if dealing

with molecules, where important symmetries that simplify the calculation in the atomic case are no longer present.

An attractive alternative to these computationally intensive methods has arisen in the form of approximate semiclassical or mixed quantum-classical approaches to the photon-excited many-body Coulomb dynamics based on simple physical pictures. In [4] the single-photon double ionization of helium has been treated by separating the photoionization process into the absorption of a photon by one of the two electrons (which was described quantum mechanically) and the subsequent single or double ionization event due to the correlated motion of the electrons (which was described classically). The ratio of double to single ionization was calculated over a wide range of photon energies, showing a good agreement with experiment. This was even more remarkable since the phase-space distribution used in that work was restricted to one spatial dimension.

An extension to this approach has been developed by Schneider *et al* [5, 6], who used the Wigner transform of a simple ansatz for the helium groundstate to calculate the statistical weights of the individual classical trajectories. Moreover, the so-called PEAK approximation which requires the photon absorption process to happen exclusively when one of the two electrons is at the nucleus restricted the integration over all initial conditions so that a three-dimensional treatment became numerically feasible. In addition, the approach has been extended to allow for the possibility of shake-off ionization, which was not included in the simpler treatment of [4]. The results from the calculations in [5] were in very good agreement with experiments, both for total and for singly differential cross sections. A first extension of this approach to three-electron atoms has been carried out recently [7].

Thus, the purpose of the present work is twofold. Methodically, we will show how to carry the ansatz of Schneider *et al* over to diatomic molecules by suitable modification and generalization of the approach. Application to the case of H_2 provides valuable further insight into the range of validity of approximate quasiclassical methods and, more generally, intuitive physical concepts such as the half-collision picture of single-photon multiple ionization described below. On the other hand, being the simplest possible two-electron molecule, H_2 can serve as a fundamental benchmark system for both numerical methods and physical understanding of correlated two-electron ejection from molecular targets in the same way that helium has become the paradigm system for the atomic case. Still, work on this system has been limited, possibly due to the increased complexity of the molecular system compared to atoms, and very few theoretical calculations of total cross sections have been reported. Early work by Le Rouzo [8, 9] has resulted in cross sections significantly larger than measured experimentally [10, 11], and first fully correlated *ab initio* calculations are only just emerging [2, 3]. Sadeghpour and Dalgarno [12] investigated the high-energy shake-off limit, but provided no data for finite photon energies. Hence, the second purpose of the present work is to provide the total double ionization cross section of H_2 over a wide range of energies extending from threshold up to several hundred eV excess energy, i.e. to the region above the cross section maximum where so far neither experimental nor theoretical results have been available, hoping that the present results will stimulate further studies in this energy range.

2. Model

2.1. General

The basic method we use for the calculation of the double ionization probability is described in great detail in [6] in the form applicable to atomic targets. For molecular targets, several new issues arise. The method is based on the so-called half-collision picture [6, 13–15] of

the double ionization process. Samson [13] observed that the ratio of double photoionization cross section to photoabsorption of a neutral atom is, over a wide energy range, proportional to the electron-impact single ionization cross section of the corresponding singly-charged ion. This led him to propose that double ionization by single-photon absorption could be viewed as a two-step process, namely the primary step of photon absorption by one electron followed by the secondary step of energy transfer from the photoelectron to the other, secondary electron. The latter step should be analogous to an electron impact ionization process, with the difference that the ‘projectile’, i.e. the photoelectron, is created inside the target. Hence, it corresponds to a *half-collision*, where the incoming half of the projectile trajectory is missing. However, in this form the picture does not include shake-off, a process which relies on the fact that initial and final states of the secondary electron are eigenstates of different Hamiltonians in the photoionization case, i.e. that the groundstate of the neutral atom is not orthogonal to the continuum of the singly-charged ion. Hence, shake-off is present in photoionization, but not in electron impact ionization. To this end, the half-collision picture has been extended by Pattard and Burgdörfer [14] by explicitly introducing an additional term to allow for shake-off. Such an approximate separation of shake-off and half-collision (or knockout) has also been used by Schneider *et al* [5], who showed that the approach leads to surprisingly good results for the description of single-photon double ionization of helium from the ground [6, 5] and also from excited [16] states. Later on, further insight into the foundation of the half-collision approach has been obtained in [15]. In the present work, we will thus follow the reasoning developed in [6, 14, 15] and employ an incoherent summation of shake-off and half-collision contributions to the double ionization. The modifications and generalizations of the ‘standard’ procedure described in [6] which are necessary for the molecular case will be developed in the following subsections.

2.2. Shake-off

It is well known that the ratio of double to single ionization following single-photon absorption does not go to zero in the high photon energy limit, but rather approaches a finite constant, the so-called shake-off limit. For two-electron atoms or ions, the corresponding expression has been given, e.g., by Åberg [17]:

$$\frac{\sigma^{2+}}{\sigma^+} \xrightarrow{E_{\text{ph}} \rightarrow \infty} \frac{O_c}{N - O_c} \quad (1)$$

or

$$\frac{\sigma^{2+}}{\sigma^{\text{abs}}} \xrightarrow{E_{\text{ph}} \rightarrow \infty} \frac{O_c}{N}, \quad (2)$$

where

$$O_c := \int |\langle \phi_f | \psi_i(\mathbf{r}_1, 0) \rangle|^2 df \quad (3)$$

and

$$N := \langle \psi_i(\mathbf{r}_1, 0) | \psi_i(\mathbf{r}_1, 0) \rangle \quad (4)$$

are the overlap with the continuum and the normalization, respectively, of the wavefunction of the secondary electron after the primary electron has absorbed a photon, which takes place at the nucleus in the high-energy limit. Here, ψ_i is the (ground) initial state of the full two-electron system and the ϕ_f are the continuum eigenstates of the corresponding one-electron Hamiltonian. In the following, we will derive the corresponding expression for H_2 . The mathematical treatment closely follows the analysis of Kabir and Salpeter [18] for the atomic transition matrix elements.

Within the usual dipole approximation, the amplitude for a transition from the initial state i to a final state f by absorption of a single photon is proportional to the corresponding dipole matrix element

$$a_{fi} \propto \langle \psi_f | \epsilon \cdot (\nabla_{\mathbf{r}_1} + \nabla_{\mathbf{r}_2}) | \psi_i \rangle, \quad (5)$$

where ϵ is the polarization direction of the photon. For large photon energies, at least one of the electrons will be high in the continuum after the photoabsorption and, hence, is well described by a simple plane wave with wavevector \mathbf{k}

$$\psi_f \rightarrow \phi_f(\mathbf{r}_1) e^{i\mathbf{k}\cdot\mathbf{r}_2} + e^{i\mathbf{k}\cdot\mathbf{r}_1} \phi_f(\mathbf{r}_2), \quad (6)$$

where we have assumed that the system is in a singlet state so that the spatial part of both initial and final states is symmetric under exchange of electrons³. Using the symmetry of ψ_i under electron exchange, this leads to

$$a_{fi} \propto 2 \langle \phi_f(\mathbf{r}_1) e^{i\mathbf{k}\cdot\mathbf{r}_2} | \epsilon \cdot (\nabla_{\mathbf{r}_1} + \nabla_{\mathbf{r}_2}) | \psi_i \rangle. \quad (7)$$

By Fourier transformation, this can be written in momentum space as

$$a_{fi} \propto 2i\sqrt{4\pi k} \langle \tilde{\phi}_f(\mathbf{p}_1) | \epsilon \cdot (\mathbf{p}_1 + \mathbf{k}) | \tilde{\psi}_i(\mathbf{p}_1, \mathbf{k}) \rangle \\ \xrightarrow{k \rightarrow \infty} 2i\sqrt{4\pi k} (\epsilon \cdot \mathbf{k}) \langle \tilde{\phi}_f(\mathbf{p}_1) | \tilde{\psi}_i(\mathbf{p}_1, \mathbf{k}) \rangle \equiv 2it_{fi}, \quad (8)$$

demonstrating that for large k the ‘exchange term’ where one electron absorbs the photon and the other leaves with a high velocity becomes negligible compared to the direct term. Using the Schrödinger equation in momentum space to replace $\tilde{\psi}_i$ in equation (8) as in [18], the leading order in $1/k$ becomes

$$t_{fi} \rightarrow \frac{-2\epsilon \cdot \mathbf{k}}{\pi^{3/2} k^{7/2}} \iint \tilde{\phi}_f^*(\mathbf{p}_1) [e^{i(\mathbf{s}-\mathbf{k})\cdot\mathbf{R}_A} \tilde{\psi}_i(\mathbf{p}_1, \mathbf{s}) + e^{i(\mathbf{s}-\mathbf{k})\cdot\mathbf{R}_B} \tilde{\psi}_i(\mathbf{p}_1, \mathbf{s})] d\mathbf{s} d\mathbf{p}_1, \quad (9)$$

where \mathbf{R}_A and \mathbf{R}_B are the position vectors of the two nuclei. An inverse Fourier transformation then leads back to coordinate space, and with $\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B$ we obtain

$$t_{fi} \rightarrow \frac{-2\epsilon \cdot \mathbf{k}}{\pi^{3/2} k^{7/2}} e^{-i\mathbf{k}\cdot(\mathbf{R}_A + \mathbf{R}_B)/2} (e^{-i\mathbf{k}\cdot\mathbf{R}/2} \langle \phi_f(\mathbf{r}_1) | \psi_i(\mathbf{r}_1, \mathbf{R}_A) \rangle + e^{i\mathbf{k}\cdot\mathbf{R}/2} \langle \phi_f(\mathbf{r}_1) | \psi_i(\mathbf{r}_1, \mathbf{R}_B) \rangle). \quad (10)$$

As in the atomic case, the asymptotic Fourier transform picks out the singularities of the Coulomb potential [19] or, physically speaking, photoabsorption takes place at one of the nuclei which has to take the recoil to balance the electronic momentum. In the present case, however, there are two nuclei and photoabsorption can take place at either one of them, the transition *amplitude* is a coherent summation of both processes which in general have different phases associated with each other. The transition *probability* thus contains an interference term

$$P_f \propto \frac{(\epsilon \cdot \mathbf{k})^2}{k^7} (|\langle \phi_f | \psi_{iA} \rangle|^2 + |\langle \phi_f | \psi_{iB} \rangle|^2 + 2 \cos(\mathbf{k}\cdot\mathbf{R}) \langle \phi_f | \psi_{iA} \rangle \langle \phi_f | \psi_{iB} \rangle), \quad (11)$$

where we have introduced the short-hand notation $\psi_{iA} = \psi_i(\mathbf{r}_1, \mathbf{R}_A)$, etc.

Equation (11) describes the probability for the transition to a specific two-electron final state $\psi_f = \phi_f e^{i\mathbf{k}\cdot\mathbf{r}_2}$. For the probability that the secondary electron ends up in a—bound or

³ The careful reader will also note that there is a slight ambiguity in our notation, since f labels both the two-electron final state ψ_f and the one-electron final state ϕ_f . Clearly, there is no one-to-one correspondence, by varying \mathbf{k} different ψ_f can contain the same ϕ_f . However, in order to keep the notation simple we do not distinguish the corresponding indices, since the meaning should be clear in all cases. The same applies for the bra–ket notation where we do not distinguish between one- and two-electron integrals.

continuum—one-electron final state ϕ_f , we have to integrate over the emission direction $\hat{\mathbf{k}}$ of the photoelectron. For the first two terms of equation (11), this leads to

$$\int (\boldsymbol{\epsilon} \cdot \hat{\mathbf{k}})^2 (|\langle \phi_f | \psi_{iA} \rangle|^2 + |\langle \phi_f | \psi_{iB} \rangle|^2) d\Omega_{\mathbf{k}} = \frac{4\pi}{3} (|\langle \phi_f | \psi_{iA} \rangle|^2 + |\langle \phi_f | \psi_{iB} \rangle|^2) \propto k^0. \quad (12)$$

For the interference term, on the other hand, we have

$$\begin{aligned} \int (\boldsymbol{\epsilon} \cdot \hat{\mathbf{k}})^2 \cos(\mathbf{k} \cdot \mathbf{R}) d\Omega_{\mathbf{k}} &= \frac{2\pi}{k^3 R^3} (k^2 R^2 2(\boldsymbol{\epsilon} \cdot \hat{\mathbf{R}})^2 \sin(kR) + kR \cos(kR) (6(\boldsymbol{\epsilon} \cdot \hat{\mathbf{R}})^2 - 2) \\ &\quad - (6(\boldsymbol{\epsilon} \cdot \hat{\mathbf{R}})^2 - 2) \sin(kR)) \\ &\xrightarrow{k \rightarrow \infty} \frac{4\pi (\boldsymbol{\epsilon} \cdot \hat{\mathbf{R}})^2 \sin(kR)}{kR} \propto k^{-1}. \end{aligned} \quad (13)$$

Hence, the contribution of the interference term decays faster than that of the other two, and the high-energy limit of the transition probability corresponds to an *incoherent* addition of two processes, namely photoabsorption at nucleus A and at nucleus B, respectively

$$P_f^{(1)} \xrightarrow{k \rightarrow \infty} \text{const} \frac{1}{k^5} (|\langle \phi_f | \psi_{iA} \rangle|^2 + |\langle \phi_f | \psi_{iB} \rangle|^2). \quad (14)$$

(At this point we have introduced the superscript (1) to explicitly emphasize that we are dealing with the probability of a one-electron final state ϕ_f of the secondary electron.) This finding is in contrast to the expression given by Sadeghpour and Dalgarno [12], whose equation (3a) corresponds to a coherent summation of the two possibilities. (Note, however, that their equation (3b) is identical to our equation (15))

In order to calculate the ratio of double to single ionization, the constant prefactors in equation (14) and the preceding equations are not needed, since we can make use of a sum rule. Summing over all bound and continuum final states ϕ_f , we obtain

$$\sum_f P_f^{(1)} = \text{const} \frac{1}{k^5} (\langle \psi_{iA} | \psi_{iA} \rangle + \langle \psi_{iB} | \psi_{iB} \rangle). \quad (15)$$

Hence, the shake-off limits for the ratio of double to single ionization and for double ionization to photoabsorption retain the form of equations (1) and (2), respectively, with the modified expressions

$$\bar{O}_c = \int (|\langle \phi_f | \psi_{iA} \rangle|^2 + |\langle \phi_f | \psi_{iB} \rangle|^2) df \quad (16)$$

and

$$\tilde{N} = \langle \psi_{iA} | \psi_{iA} \rangle + \langle \psi_{iB} | \psi_{iB} \rangle \quad (17)$$

for overlap and normalization.

2.3. Half-collision

In principle, the half-collision contribution to the double ionization probability can be calculated with any method available for electron impact ionization calculations. For example, Pattard and Burgdörfer [14, 20] used a first-order Born approximation in connection with the calculation of triple ionization of lithium, which led to satisfying results at high photon energies but, not surprisingly, failed at lower energies. On the other hand, Schneider *et al* [5] have employed classical trajectory Monte Carlo (CTMC) calculations for the description of the half-collision cross section, which for atomic targets has proven to lead to surprisingly accurate results over the whole energy range. Therefore, in the following we will adopt their

approach which, however, has to be adapted to the molecular case which introduces additional complications, described in detail in the remainder of this section.

The method of Schneider *et al* as applicable for atoms is described in detail in [6]. Briefly, the photoelectron is placed at the nucleus (where photoabsorption will take place at least in the high-energy limit) while the initial conditions for the second electron are chosen according to an ‘energy restricted’ Wigner distribution. The latter corresponds to the initial-state (i.e. *before* the photoabsorption) wavefunction of the electron, restricted, however, to an energy shell corresponding to an effective one-particle energy according to its initial binding energy in the atom. As Heller [21] has pointed out, it is in general *not* a good approximation to naively replace the exact quantum evolution of the Wigner distribution with its classical counterpart. Moreover, the restriction of the initial phase-space distribution to a subspace of fixed energy introduces another severe approximation, so that the success of this method in the case of helium double ionization is rather remarkable. It seems certainly worthwhile to study this point in greater detail; however, this is beyond the scope of the present paper.

In the applications to the helium ground [5] and singly excited [16] states treated so far, this prescription was sufficient to specify the initial conditions for the calculation of the half-collision contribution to the double ionization cross section. This is due to the fact that only s-states are involved in these cases, i.e. the initial electronic wavefunctions are spherically symmetric. Hence, the anisotropic emission pattern of the photoelectron plays no role for the calculation of the half-collision since all emission angles of the photoelectron with respect to the photon polarization axis give equal contributions to the ratio of double to single ionization. This situation changes when other, non-spherically-symmetric excited atomic states (such as, e.g., 1s2p) are considered or generally in molecules, where the molecular axis introduces a breaking of the spherical symmetry. In this case, not only the photoabsorption in the first place, but also the energy transfer from photoelectron to secondary electron through the half-collision will depend on the orientation of the molecular axis with respect to the photon polarization axis, and a suitable averaging has to be performed.

In principle, one could lift the PEAK approximation (i.e. the assumption that the photoelectron takes off from the nucleus) employed by Schneider *et al* and choose initial conditions according to the full two-electron Wigner distribution, only restricted to the final-state (total) energy shell. However, this means that, for a fixed direction of the molecular axis with respect to the photon polarization direction, an 11-dimensional phase-space integral has to be evaluated, which then in addition will have to be averaged over all molecular orientations. Thus, the high-dimensionality of the corresponding phase space makes this straightforward approach prohibitively expensive in terms of the required numerical effort. We thus chose to retain as many of the additional simplifications introduced by Schneider *et al* as possible. More precisely, the procedure adopted for the calculation of the half-collision process is the following: we represent the initial (ground) state of the hydrogen molecule by a product of two H_2^+ -LCAO wavefunctions

$$\begin{aligned}\psi_i(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{\sqrt{N}}(\phi_A(\mathbf{r}_1) + \phi_B(\mathbf{r}_1))(\phi_A(\mathbf{r}_2) + \phi_B(\mathbf{r}_2)) \\ &\equiv \phi(\mathbf{r}_1)\phi(\mathbf{r}_2),\end{aligned}\tag{18}$$

where $\phi_{A/B}$ is a hydrogenic 1s wavefunction with an effective nuclear charge $Z_{\text{eff}} = 1.194$ (this choice of Z_{eff} minimizes the variational groundstate energy) centred around $\mathbf{R}_{A/B}$, the position of the nuclei. We further assume that electron 1 will be the photoelectron and electron 2 will be the remaining one. The opposite case where electron 2 absorbs the photon leads to identical matrix elements, hence a correct symmetrization only leads to a constant factor in all

transition probabilities which drops out when the ratio of double ionization to photoabsorption is considered. Following the argument and notation of [15], we can then consider

$$\psi_{\text{abs}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{(\partial_{z_1} \psi_i)}{\sqrt{((\partial_{z_1} \psi_i) | (\partial_{z_1} \psi_i))}} \quad (19)$$

as the wavefunction after the molecule has absorbed the photon (which assumes that the dipole approximation has been employed for the photon and that the photon is linearly polarized in the z direction). This wavefunction serves as the input for the two-electron Wigner distribution which determines the weights of the classical trajectories leading to single or double ionization, respectively.

First of all, with

$$\psi_{\text{abs}}(\mathbf{r}_1, \mathbf{r}_2) \propto (\partial_{z_1} \phi(\mathbf{r}_1)) \phi(\mathbf{r}_2) \equiv \phi_{\text{abs}}(\mathbf{r}_1) \phi(\mathbf{r}_2) \quad (20)$$

we note that the Wigner function for the two-electron wavefunction after photoabsorption factorizes:

$$\begin{aligned} W_{\text{abs}}(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2) &= \int d\eta_1 d\eta_2 \psi_{\text{abs}}^* \left(\mathbf{r}_1 - \frac{\eta_1}{2}, \mathbf{r}_2 - \frac{\eta_2}{2} \right) \psi_{\text{abs}} \left(\mathbf{r}_1 + \frac{\eta_1}{2}, \mathbf{r}_2 + \frac{\eta_2}{2} \right) e^{i(\mathbf{p}_1 \cdot \eta_1 + \mathbf{p}_2 \cdot \eta_2)} \\ &\equiv w_{\text{abs}}(\mathbf{r}_1, \mathbf{p}_1) w(\mathbf{r}_2, \mathbf{p}_2). \end{aligned} \quad (21)$$

As we employ the PEAK approximation, the initial \mathbf{r}_1 is fixed to be either \mathbf{R}_A or \mathbf{R}_B ; the absolute value of the corresponding momentum is infinite, but in regularized coordinates [6] it is fixed by the total energy of the system. Hence, we are only interested in the angular distribution $P(\theta_{p_1}, \phi_{p_1})$ with which electron 1 leaves one of the nuclei. Since $w_{\text{abs}}(\mathbf{r}_1, \mathbf{p}_1) \rightarrow 0$ as $\mathbf{r}_1 \rightarrow \mathbf{R}_{A/B}$ and $|\mathbf{p}_1| \rightarrow \infty$, we cannot simply extract the angular distribution directly from the Wigner function. Thus, we are forced to relax the PEAK approximation when calculating $P(\theta_{p_1}, \phi_{p_1})$. From the well-known property of the Wigner function that integrating over the spatial coordinate yields the quantum-mechanical probability distribution for the momentum, the *full*⁴ probability distribution for \mathbf{p}_1 ,

$$P_{\text{full}}(p_1, \theta_{p_1}, \phi_{p_1}) := \int w_{\text{abs}}(\mathbf{r}_1, \mathbf{p}_1) d\mathbf{r}_1 = |\tilde{\phi}_{\text{abs}}(\mathbf{p}_1)|^2, \quad (22)$$

is simply given by the Fourier transform of ϕ_{abs} ,

$$\tilde{\phi}_{\text{abs}}(\mathbf{p}_1) \propto \langle \exp(i\mathbf{p}_1 \mathbf{r}_1) | \partial_{z_1} | \phi(\mathbf{r}_1) \rangle. \quad (23)$$

$\tilde{\phi}_{\text{abs}}(\mathbf{p}_1)$ can be analytically calculated, so that we finally get

$$P_{\text{full}}(p_1, \theta_{p_1}, \phi_{p_1}) \propto |\tilde{\phi}_0(p_1) p_1 \cos \theta_{p_1} 2 \cos(\mathbf{p}_1 \cdot (\mathbf{R}_A - \mathbf{R}_B)/2)|^2 \quad (24)$$

with $\tilde{\phi}_0$ the momentum-space wavefunction of the hydrogenic groundstate. The only remaining question is which value of p_1 should be used in order to extract $P(\theta_{p_1}, \phi_{p_1})$. Since $\tilde{\phi}_{\text{abs}}(\mathbf{p}_1)$ is a projection of $\phi_{\text{abs}}(\mathbf{r}_1)$ onto plane waves, $|\tilde{\phi}_{\text{abs}}|^2$ can also be understood as the probability for the photoelectron to acquire a momentum \mathbf{p}_1 after photoabsorption if there were no interaction with the nuclei and the second electron in the final state. Hence, in determining the angular distribution of the photoelectron,

$$P(\theta_{p_1}, \phi_{p_1}) \propto P_{\text{full}}(p_1, \theta_{p_1}, \phi_{p_1}) \Big|_{p_1=p_1^*(E_{\text{ph}})}, \quad (25)$$

we choose $p_1^*(E_{\text{ph}}) = \sqrt{2(E_b/2 + E_{\text{ph}})}$ which is the asymptotic momentum of an electron with an initial binding energy that is half of $E_b = -51.08$ eV, the total electronic binding energy.

⁴ One may argue that this should lead to an at least equally appropriate estimate of the ‘true’ angular distribution at finite excess energies, since the PEAK approximation is only employed for numerical convenience and the electron may come from any point in space.

The remaining distribution for \mathbf{r}_2 and \mathbf{p}_2 is more straightforward. Here, we can directly take $w(\mathbf{r}_2, \mathbf{p}_2)$, with the only constraint being $E_2 = E_b/2$, i.e. restricted to a one-particle energy shell as in [5]. E_2 is taken to be

$$E_2(\mathbf{r}_2, \mathbf{p}_2) = \frac{\mathbf{p}_2^2}{2} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_A|} - \frac{1}{|\mathbf{r}_2 - \mathbf{R}_B|} + \int \frac{|\phi(\mathbf{r}_1)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1, \quad (26)$$

i.e. the interaction with the first electron is included on a mean-field level.

Finally, one has to take into account that the probability for *photoabsorption* depends on the angle between the molecular axis and the polarization direction as $(1 + \beta_m(E_{\text{ph}})P_2(\epsilon \cdot \hat{\mathbf{R}}))$ with an energy-dependent beta parameter β_m which we take as external input [22]. Summing everything up, the weight function for our classical ensemble reads

$$\mathcal{P}(\theta_{p_1}, \phi_{p_1}, \mathbf{r}_2, \mathbf{p}_2, \hat{\mathbf{R}}) = (1 + \beta_m(E_{\text{ph}})P_2(\epsilon \cdot \hat{\mathbf{R}}))P(\theta_{p_1}, \phi_{p_1})w(\mathbf{r}_2, \mathbf{p}_2)\delta(E_2 - E_b/2). \quad (27)$$

The probability for a certain final state where the first electron has an energy E_1^f and the second electron has an energy E_2^f (we can unambiguously assign energies to both electrons in the final state since there the interaction between them is zero in the case of single as well as double ionization) is finally given by

$$p(E_1^f, E_2^f) = \frac{1}{2} \int \mathcal{P}(\theta_{p_1}, \phi_{p_1}, \mathbf{r}_2, \mathbf{p}_2, \hat{\mathbf{R}}) (\delta(\mathbf{r}_1 - \mathbf{R}_A) + \delta(\mathbf{r}_1 - \mathbf{R}_B)) \delta(E_1^f - E_1(\mathbf{r}_1^f, \mathbf{p}_1^f)) \\ \times \delta(E_2^f - E_2(\mathbf{r}_2^f, \mathbf{p}_2^f)) \delta(E_b + E_{\text{ph}} - E_1^f - E_2^f) d\mathbf{r}_1 d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 d\hat{\mathbf{R}}. \quad (28)$$

3. Results

3.1. Shake-off

The asymptotic shake-off value has been calculated using equation (2) with \tilde{O}_c and \tilde{N} , as derived in the previous section. The overlap matrix elements are conveniently calculated in prolate spheroidal coordinates $\lambda = (|\mathbf{r} - \mathbf{R}_A| + |\mathbf{r} - \mathbf{R}_B|)/|\mathbf{R}_A - \mathbf{R}_B|$, $\mu = (|\mathbf{r} - \mathbf{R}_A| - |\mathbf{r} - \mathbf{R}_B|)/|\mathbf{R}_A - \mathbf{R}_B|$. For the groundstate wavefunction ψ_i , we use the correlated wavefunction given in [23]. The final-state wavefunctions ϕ_f have been calculated by numerically solving the eigenvalue problem, which is separable in prolate spheroidal coordinates. Bound as well as continuum states have been obtained, where the continuum has been discretized via box-quantization, i.e. by restricting $\lambda < \lambda_{\text{max}}$ and requiring Dirichlet boundary conditions at λ_{max} . The box size was varied to ensure convergence of the result. Moreover, the lowest bound states have been compared to the wavefunctions tabulated in the literature [24], showing good agreement of the overlap matrix elements. Our results are summarized in table 1, which shows the probability that the secondary electron is shaken into the final state ϕ_{n_μ, n_λ} ,

$$P_{n_\mu, n_\lambda} = \frac{(|\langle \phi_{n_\mu, n_\lambda} | \psi_{iA} \rangle|^2 + |\langle \phi_{n_\mu, n_\lambda} | \psi_{iB} \rangle|^2)}{(\langle \psi_{iA} | \psi_{iA} \rangle + \langle \psi_{iB} | \psi_{iB} \rangle)}, \quad (29)$$

where n_μ and n_λ are the number of nodes in the μ - and λ -wavefunction, respectively (as noted in [12], only sigma-states with $m = 0$ produce nonvanishing overlap matrix elements, hence we omit the quantum number labelling the projection of the angular momentum on the internuclear axis in labelling the final ionic states). Taking into account final states up to $n_\mu = 5$, the probability to be shaken into a continuum state is found to be 7.015×10^{-3} , making the asymptotic double-to-single ionization ratio $R = \sigma^{2+}/\sigma^+ = 7.065 \times 10^{-3}$. This is in contrast to the result of [12], which was given as $R = 0.0225$. On the other hand, comparing the shake probabilities for individual states, the present results closely match those of [12].

Table 1. Shake probabilities into some selected final states, n_μ and n_λ are the number of nodes in the μ - and λ -wavefunction, respectively.

n_μ	n_λ	P_{n_μ, n_λ}	n_μ	n_λ	P_{n_μ, n_λ}	n_μ	n_λ	P_{n_μ, n_λ}
0	0	0.930 79	1	0	1.46×10^{-2}	2	0	3.27×10^{-6}
0	1	3.97×10^{-2}	1	1	9.97×10^{-4}	2	1	4.49×10^{-7}
0	2	3.61×10^{-3}	1	2	2.64×10^{-4}	2	2	1.61×10^{-7}
0	3	1.14×10^{-3}	1	3	1.12×10^{-4}	2	3	7.98×10^{-8}
0	4	5.18×10^{-4}	1	4	5.88×10^{-5}	2	4	4.65×10^{-8}
0	5	2.83×10^{-4}	1	5	3.50×10^{-5}	2	5	2.98×10^{-8}
0	6	1.72×10^{-4}	1	6	2.26×10^{-5}	2	6	2.03×10^{-8}
0	7	1.13×10^{-4}	1	7	1.54×10^{-5}	2	7	1.45×10^{-8}
0	8	7.87×10^{-5}	1	8	1.11×10^{-6}	2	8	1.07×10^{-8}
0	9	5.69×10^{-5}	1	9	8.19×10^{-6}	2	9	8.21×10^{-9}
\sum_{bnd}		0.976 76	\sum_{bnd}		1.62×10^{-2}	\sum_{bnd}		4.13×10^{-6}
\sum_{cont}		5.50×10^{-3}	\sum_{cont}		1.42×10^{-3}	\sum_{cont}		9.25×10^{-5}

The discrepancy between the final results can be traced to the fact that the authors of [12] argue that only gerade states of H_2^+ can be populated in the final state. However, this is not the case in the *incoherent* sum of transition probabilities derived in the previous section (equation 14). Mathematically, this is seen from equation (11), where the interference term depends on the direction of \mathbf{k} , i.e. of the outgoing photoelectron. Physically, it means that the initial symmetry of the full two-electron problem does not allow conclusions about the symmetry of the restricted one-electron system since the plane wave of the outgoing photoelectron does not have a well-defined parity.

Including final states up to $n_\mu = 5$, we find the sum of all individual probabilities P_{n_μ, n_λ} to add up to 0.999 9917. In principle, of course, the sum over all final states has to add up to 1. Hence, we conclude that the numerical error of our calculation should be no larger than 10^{-4} . Moreover, we suggest that the result of [12] is incorrect due to the omission of the ungerade-type final states. There, R has been obtained in an indirect way by exploiting a completeness argument and expressing P_{cont} as $1 - P_{\text{bound}}$; however, from the present calculation it is clear that the calculated values for the (bound *plus* continuum) gerade states only do not add up to 1.

At this point, it is worthwhile to compare the H_2 shake-off limit to that of He, i.e. to that of the corresponding *atomic* two-electron system. For He, R has been found to be 0.0164, which is significantly larger than the present value for H_2 . This seems plausible in view of the fact that it is the correlation in the initial two-electron state which is responsible for the shake-off process. For a molecule, the electronic clouds are more delocalized since they are localized on two spatially separated nuclei. Hence, one might intuitively expect less electron–electron correlation in the molecular groundstate than in the atomic groundstate, leading to a smaller change in the effective one-electron potential for the secondary electron once the photoelectron is removed, thus leading to a smaller probability for shake-off.

While shake-off is well defined in the asymptotic high-energy limit, its meaning at finite energies is less clear and has been the subject of debate recently [15, and references therein]. In [15], it was argued that a satisfactory ‘operational’ definition of shake-off at a finite energy E is the one introduced in [5], namely

$$P_f^{(1)}(E) = P_f^{(1)}(\infty)\theta(E - E_1^f), \quad (30)$$

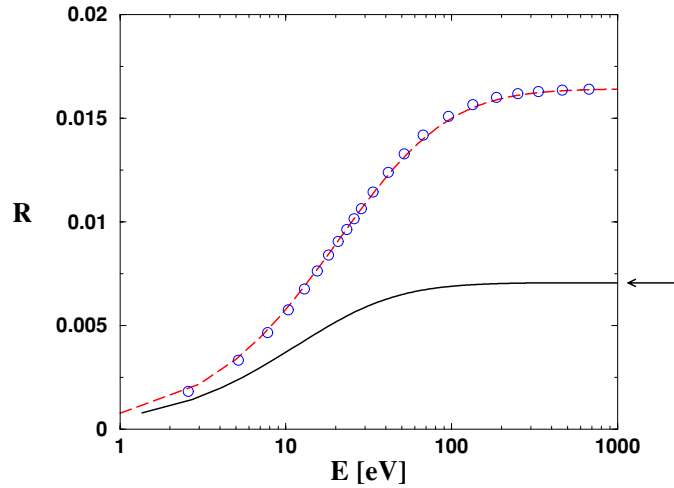


Figure 1. Energy dependence of the shake-off contribution to the cross section ratio σ^{2+}/σ^+ . The full curve shows the present calculation for H_2 , the dashed curve the corresponding result for He. The open circles are a scaled version of the H_2 data (see the text for explanation). Finally, the arrow marks the asymptotic high-energy limit.

where $P_f^{(1)}(\infty)$ is the asymptotic shake-off probability for reaching a final state ϕ_f , E_1^f is the energy of the final state ϕ_f and θ is the unit step function. In the present case, $P_f^{(1)}(\infty)$ is given by equation (14). However, in contrast to the atomic case considered previously, the derivation of equation (14) requires the limit of high photon energies not only in justifying that photoabsorption takes place at one of the nuclei, but also in order to omit the interference term in the transition probability which is still present in equation (11). Hence, one may argue that this interference term should be taken into account for the calculation of shake-off probabilities at finite energies. Doing so leads to oscillations in the shake-off double-to-single ionization ratio R superimposed on the smooth behaviour given by equation (30) and depicted in figure 1. However, we argue that these oscillations would be an artefact of an inconsistent use of the limit $k \rightarrow \infty$ for the momentum k of the photoelectron. Use of equation (11) for finite energies leads, e.g., to the same divergencies for $k \rightarrow 0$ as equation (14) due to the $1/k^5$ prefactor, hence it cannot be attributed a rigorous meaning beyond the limit $k \rightarrow \infty$ in which it was derived. Hence, we use equation (30) for the calculation of shake-off at finite energies. A more consistent description omitting the limit $k \rightarrow \infty$ could only be achieved by calculating two-electron overlap integrals, i.e. going back to equation (14) of [15]. In this case, we believe that oscillations due to interferences would probably be washed out in the total cross section due to the averaging over k involved in the integration over final states.

The energy dependence of the shake-off contribution to the cross section ratio resulting from equation (30) is shown in figure 1, where it is also compared to the corresponding curve for He. Coming from the high-energy limit, the shake-off probability stays almost constant down to about 50 eV excess energy, below which it rapidly drops down. (The excess energy $E = E_{\text{ph}} - I^{2+}(R_0)$ is the difference between the photon energy and the double ionization potential for a fixed internuclear distance R_0 corresponding to the H_2 groundstate.) Compared to He, this decay happens on a significantly smaller energy scale, in other words, the shake-off probability approaches its asymptotic value already at smaller excess energies. The open circles in figure 1 show a scaled version of the H_2 data, obtained by the similarity

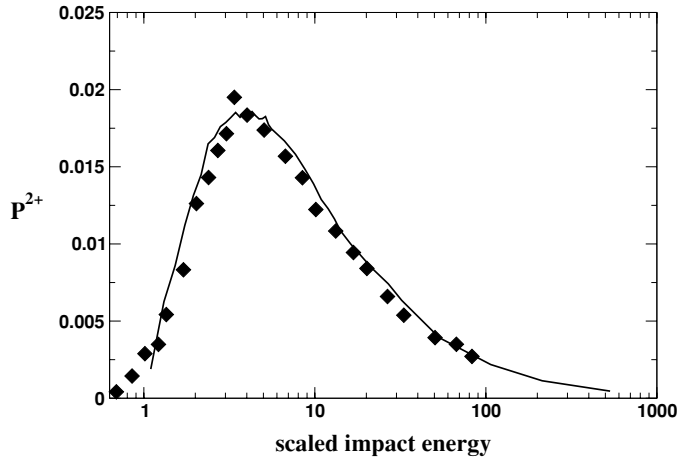


Figure 2. Knockout probability (solid line, this work) and experimental electron impact ionization cross section of H_2^+ (diamonds, from [25]) as a function of the impact energy scaled by the binding energy (see text). In order to compare the knockout *probability* calculated here to the *cross section* measured experimentally, the latter has been normalized by a constant factor.

transformation $R \rightarrow R \times R_{\infty}^{\text{He}}/R_{\infty}^{\text{H}_2}$, $E \rightarrow 1.9 \times E$. As can be seen, the shape of the H_2 curve closely matches that of the He case if both axes are scaled appropriately. The scaling of the absolute magnitude of R , as discussed above, should represent the amount of electron-electron correlation in the initial state. The scaling factor for the energy axis has been set ‘by hand’ to obtain a good visual fit to the He data. Usually, ionization cross sections roughly scale with the corresponding binding energy of the initial state. In the present case such a simple argument does not explain the scaling factor, which may not be too surprising since the shape of the electronic clouds is different in the molecular and atomic case, respectively, so that a simple scaling based on, e.g., effective charges cannot be applied. We have not been able to find a straightforward explanation for the energy scaling factor of about 1.9. Nevertheless, the great similarity of the shape of the shake-off probability for the two cases seems remarkable, and it seems unlikely that this similarity is just by accident.

3.2. Half-collision

For each photon energy E_{ph} , 10^6 trajectories were calculated and $p(E_1^f, E_2^f)$ (equation (28)) was added to p^+ or p^{2+} , respectively. The resulting $P^{2+} \equiv p^{2+}/(p^+ + p^{2+}) \equiv \sigma^{2+}/(\sigma^+ + \sigma^{2+})$ is shown in figure 2 as a function of the scaled ‘impact’ energy of the system, defined as $\epsilon_{\text{imp}} = E_{\text{imp}}/E_{\text{bind}}$. (The scaling of energies by the binding energy of the ‘target’ system has been introduced in [6] to account for the fact that cross sections typically scale with this binding energy, which is different in the case of electron impact ionization and half-collision due to partial screening of the electron–nucleus interaction in the latter case.) Within the half-collision picture, the ‘impact energy’ E_{imp} for H_2 photoionization is the photon energy minus the binding energy E_1^i of the primary electron, while E_{bind} is the binding energy E_2^i of the secondary electron. Assuming equivalent electrons in the H_2 groundstate, we set $E_1^i = E_2^i = E_b/2$. Then, from the idea of the half-collision picture, P^{2+} should be proportional to the electron impact single ionization cross section of the H_2^+ ion. The latter has recently been measured experimentally [25], and has also been calculated numerically [26]. Both the experiment and the numerical results agree well with the earlier measurement

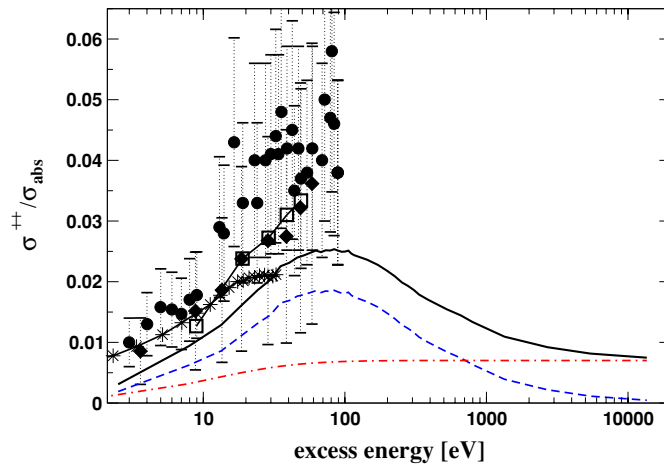


Figure 3. Single-photon double ionization of H_2 : ratio of double ionization to total photoabsorption. Shown are the shake-off (dot-dashed curve) and knockout (dashed) contributions, as well as the incoherent sum of both (solid curve). Solid symbols with error bars are experimental results from [10] (circles) and [11] (diamonds), connected open symbols show recent calculations from [2] (squares) and [3, velocity gauge result] (stars). For [2, 3, 11], we have divided their double ionization cross sections by the photoabsorption cross section given in [10] in order to obtain the ratio. Note that this may introduce an additional error in these data.

of Peart and Dolder [27], showing the maximum of the ionization cross section at an excess energy of roughly 70 eV. The experimental results from [25] have been included in figure 2 with the energy of the impacting electron scaled by the binding energy of the target electron, $E_{\text{bind}} = 29.97$ eV. The similarity between the two curves is striking, especially if one considers the fact that not only the binding energies of the two targets are different (this part has been approximately taken into account by using the scaled energy) but also the internuclear distances of H_2^+ in the electron impact ionization experiment and of the ‘target’ H_2 in the half-collision process, where one of the electrons plays the role of the projectile, are not identical. At very small energies, discrepancies between the two cases can be observed, where the experiment shows a significant amount of ionization below the ‘threshold’ energy $\epsilon_{\text{imp}} = 1$. This may to a small extent be attributed to the role of nuclear motion at these low energies, since $E_{\text{bind}} = 29.97$ eV is the binding energy for fixed internuclear distance and the ‘real’ threshold energy is obtained by taking into account the Coulomb repulsion between the nuclei. However, since the nuclei are so much heavier than the electrons, their motion should only play a role very close to threshold. More likely, the high cross section at these low energies comes from the distribution of vibrational states (equivalent to a distribution of binding energies) which has been used in the experiment [25]. The distribution of vibrational states extended up to $\nu = 11$, which can shift the energetic difference between the potential curves in the electronic ground state and in the Coulomb explosion channel by more than 10 eV.

3.3. Double ionization

In figure 3, we show the ratio of double ionization to total photoabsorption, calculated by using the incoherent sum of the shake-off and knockout contribution as discussed above. The results of the experiments [10, 11] are also included in the figure, as well as the two recent calculations [2, 3]. Both sets of experimental data suffer from large error bars and the fact

that the available photon energies were not high enough to obtain data beyond the maximum of the ratio around 80 eV. Our results are systematically lower than the experimental data of Kossmann *et al*, and significantly lower than those of Dujardin *et al*, but well within the error bars of at least the former experiment. Compared to the *ab initio* calculations, our findings again indicate a somewhat lower ratio than it has been found in [2, 3]. Also in these theoretical calculations, however, the photon energy has not been extended to large enough values to compare characteristic properties of the shape of the ratio like the maximum or the high-energy limit. As our data suggest, both shake-off and knockout double ionization are smaller than in the corresponding atomic system helium, which might be attributed to the fact that the two-centre nature of the molecular groundstate leads to less strongly correlated electrons. Moreover, we would predict that double ionization is dominated by collision-type processes up to at least 500 eV excess energy, in contrast to helium where both mechanisms are comparable around 200 eV and shake-off becomes the dominant process already around 300 eV above threshold. We may speculate that this is again an evidence for the smaller amount of correlation in the molecular groundstate, since this strong correlation is more important for shake processes than for collision processes. The latter can still be relatively efficient in ionizing the secondary electron, even if the photoelectron ‘misses’ the second electron in half of its outgoing trajectories.

In view of the scarcity of experimental as well as theoretical results covering a rather small energy range, and given the fact that the experimental data have been obtained more than 15 years ago, a judgement of the quality of our calculations is difficult. In the high-energy limit, where the knockout contribution goes to zero and the shake-off approximation becomes exact, our calculations can be expected to become exact. For low to intermediate photon energies, it is not *a priori* clear whether our method, which was empirically shown to work very well for two-electron atoms, still gives good results in the molecular case. To answer this question has been part of the motivation for this paper. Certainly, a comparison of our results with the available data shows a satisfying agreement, given the relative simplicity of the calculation and the underlying physical picture. In order to say more (e.g., concerning the incoherent summation of shake-off and knockout employed in our model) further experiments and calculations on this benchmark molecular system have to be performed, especially at higher energies where our calculation provides the first data obtained so far. New experiments are planned in the near future in the group of Dörner [28], which, due to the advances in experimental technologies in recent years, can be expected to yield results with significantly smaller error bars than the data shown here. Hopefully, the present work together with the prospect of new experiments will also stimulate further theoretical work. Until such new results become available, the predictions made by our model concerning the position of the maximum and the shake-off limit await verification.

4. Conclusions and outlook

In the present work we have formulated a mixed quantum-classical approach for the calculation of single-photon double ionization of diatomic molecules. Applying this approach to molecular hydrogen, we have analysed the role of shake-off and knockout, respectively, in molecular photoionization. We could show that both are smaller in H₂ than in helium, which may be attributed to smaller electron–electron correlation in the molecular groundstate. The knockout process can be well described by a half-collision process, as indicated by the proportionality of the knockout probability to the cross section for electron impact ionization of H₂⁺. The incoherent summation of shake-off and knockout yields satisfactory agreement with the available theoretical and experimental data. Moreover, the current work provides the first

data for the double ionization cross section at energies above the cross section maximum. Overall, the approach presented here can be considered a valuable alternative to much more involved *ab initio* calculations of molecular double photoionization.

A natural extension of the present work would be to calculate angular differential cross sections, where the amount of available data is larger than for the total cross section, and the validity of our model would be put to a much more severe test. Unfortunately, the number of trajectories that is needed in order to get converged results for angular differential cross sections is easily one order of magnitude higher than in the present work, so that such calculations will have to be part of future investigations. Still, we hope that the present work will stimulate further experimental and theoretical investigations on this most simple molecular target system.

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References

- [1] Walter M and Briggs J S 1999 *J. Phys. B: At. Mol. Opt. Phys.* **32** 2487
- [2] Colgan J, Pindzola M S and Robicheaux F 2004 *J. Phys. B: At. Mol. Opt. Phys.* **37** L377
- [3] Vanroose W, Martín F, Rescigno T N and McCurdy C W 2004 *Phys. Rev. A* **70** 050703
- [4] Rost J M 1996 *Phys. Rev. A* **53** R640
- [5] Schneider T, Chocian P and Rost J M 2002 *Phys. Rev. Lett.* **89** 073002
- [6] Schneider T and Rost J M 2003 *Phys. Rev. A* **67** 062704
- [7] Emmanouilidou A and Rost J M 2004 *Preprint physics/0409034*
- [8] Le Rouzo H 1986 *J. Phys. B: At. Mol. Phys.* **19** L677
- [9] Le Rouzo H 1988 *Phys. Rev. A* **37** 1512
- [10] Dujardin G, Besnard M J, Hellner L and Malinovitch Y 1987 *Phys. Rev. A* **35** 5012
- [11] Kossmann H, Schwarzkopf O, Kämmerling B and Schmidt V 1989 *Phys. Rev. Lett.* **63** 2040
- [12] Sadeghpour H R and Dalgarno A 1993 *Phys. Rev. A* **47** R2458
- [13] Samson J A R 1990 *Phys. Rev. Lett.* **65** 2861
- [14] Pattard T and Burgdörfer J 2001 *Phys. Rev. A* **64** 042720
- [15] Pattard T, Schneider T and Rost J M 2003 *J. Phys. B: At. Mol. Opt. Phys.* **36** L189
- [16] Emmanouilidou A, Schneider T and Rost J M 2003 *J. Phys. B: At. Mol. Opt. Phys.* **36** 2717
- [17] Åberg T 1969 *Ann. Acad. Sci. Fenn. AVI* **308** 1
- [18] Kabir P K and Salpeter E E 1957 *Phys. Rev.* **108** 1256
- [19] Surić T, Drukarev E G and Pratt R H 2003 *Phys. Rev. A* **67** 022709
- [20] Pattard T and Burgdörfer J 2001 *Phys. Rev. A* **63** 020701(R)
- [21] Heller E J 1976 *J. Chem. Phys.* **65** 1289
- [22] Zimmermann B 2003 Private communication
- [23] James H M and Coolidge A S 1933 *J. Chem. Phys.* **1** 825
- [24] Bates D R, Ledsham K and Steward A L 1953 *Phil. Trans. R. Soc.* **246** 215
- [25] Abdellahi El Ghazaly M O, Jureta J, Urbain X and Defrance P 2004 *J. Phys. B: At. Mol. Opt. Phys.* **37** 2467
- [26] Robicheaux F 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 779
- [27] Peart B and Dolder K T 1973 *J. Phys. B: At. Mol. Phys.* **6** 2409
- [28] Dörner R 2004 Private communication