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Stimulated Raman transitions from the metastable 2s state of hydrogen

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Abstract

We consider the hydrogen atom \( \text{H}(2s) \) exposed to a short laser pulse with a central frequency \( \omega_0 \) ranging from 136 eV to 1.5 keV (\( \omega_0 \approx 5–55 \text{ au} \)) at the intensity of \( 3.51 \times 10^{16} \text{ W cm}^{-2} \). We study stimulated Raman scattering transitions to the \( 1s \) ground state (anti-Stokes) and to the upper \( ns, np \) and \( nd \) states (with \( n > 2 \)) (Stokes). Nondipole (retardation) effects are included up to \( \mathcal{O}(1/c) \) (\( c \) is the speed of light in a vacuum). The calculation of the transition probabilities, based on the integration of the time-dependent Schrödinger equation, is confronted with results obtained by applying perturbation theory. The two methods are in very good agreement. We show that retardation effects play an important role for frequencies \( \omega_0 \) larger than a few hundred eV and pulse durations of the order of the femtosecond. In this regime, as the frequency \( \omega_0 \) increases, the contribution of the \( A^2 \) term dominates over \( A \cdot P \) (where \( A \) and \( P \) denote the vector potential of the field and the momentum operator, respectively). Results are presented for various values of the pulse frequency and duration.

Keywords: stimulated Raman scattering, nondipole effects, xuv and x-ray, free electron laser

(Some figures may appear in colour only in the online journal)

1. Introduction

The study of the hydrogen atom interacting with external fields played a key role in the progress of atomic physics: the spectroscopy confirmed the first calculations of emission and absorption spectra [1], the measurement of second-order Stark effect [2] was a decisive step in favor of Schrödinger quantum mechanics in contrast with the old quantum theory, the experimental research oriented towards the detection of the fine structure in spectral lines or the measurement of the Lamb shift led to a continuous improvement of the methods and technical apparatus in use.

Radiation scattering is a powerful method for the investigation of atoms and molecules interacting with light, with major practical applications. In the case of an atom prepared in an excited metastable state, radiation scattering makes possible the decay of the state by anti-Stokes Raman transitions.

The metastable \( 2s \) state of hydrogen has continuously received a special attention, it is involved in a variety of fundamental experiments. The \( 2s \) state of the isolated atom, with a lifetime of approximately \( 1/7 \) s, decays spontaneously by two-photon emission. In 1931 Maria Goeppert-Mayer [3] described the two-photon emission as the main decay mechanism of the metastable \( 2s \) state of hydrogen. Her calculation, using the second-order perturbation theory in the framework of the quantum theory of radiation developed by Dirac, marked a milestone in the study of radiative processes. Apart from this, for almost three decades the main practical interest was connected with astrophysical observations [4]. The presence of external electromagnetic radiation induces a pair of two-photon processes contributing to the quenching of the state: the stimulated emission process and the anti-Stokes Raman \( 2s \rightarrow 1s \) transition.

Around 1960 it was realized that the laser development will make possible to study effects not observable until then. Zernik envisaged a program of theoretical and experimental investigations that he started with calculations on the optical quenching of metastable hydrogen interacting with a ruby
laser [5, 6]. He applied the technique introduced by Schwartz and Tiemann [7], already used by Mittleman and Wolf for their calculation of Rayleigh scattering on hydrogen [8]. Soon after that, Zernik published his results on the ionization of atomic hydrogen [9].

The first laboratory study of the $2s \rightarrow 1s$ transition, done with ionized helium, is due to Novick and coworkers [10]. In 1970 Braunlich and Lambropoulos reported the observation of singly stimulated two-photon emission from the metastable $2s$ state of the deuterium atom [11] and then, for the same atom, the emission of an anti-Stokes Raman photon, the other stimulated mode of decay of the metastable state in the presence of intense electromagnetic radiation [12]. They used a Nd–glass laser radiation with a photon frequency of 1.17 eV, details on the experimental work and the theory of both decay mechanisms were given in [13]. Another interest in two-photon decays is connected with the experimental observation of its contribution in the mechanism of filling inner-shell vacancies in atoms [14–16].

In the last years the development of coherent, tunable, x-ray free electron lasers (FELs) opened the way to the exploration of new regimes in laser–matter interactions, with the perspective of applications in physics, chemistry and biology. One of the most interesting aspect of FELs is the production of femtosecond x-ray pulses at high intensity [17–20] allowing the observation of nonlinear processes at short wavelengths [21]. In parallel, with the increasing power of the computers, it has been possible to perform extensive calculations for two-photon and higher-order processes for the case of hydrogen atom (or more complex atomic system) interacting with electromagnetic radiation. Also, following the development of intense lasers with short pulse duration in the eighties, more realistic descriptions of the laser–atom interaction, including the temporal dependence of the field (i.e., the laser bandwidth), have been adopted. The studies of one-active-electron systems, from which one can expect nearly exact theoretical descriptions, continue to be a guideline for the investigation of fundamental processes.

Recently we have considered stimulated Raman scattering (SRS) from the ground state of hydrogen [22, 23] due to the interaction with a radiation pulse; the process involves two frequencies ($\omega_1$ and $\omega_2$ with $\omega_1 > \omega_2$) that are non-negligible components of the pulse Fourier transform. After absorption of $\omega_1$ and emission of $\omega_2$ the hydrogen atom reaches an excited state. We have shown that SRS is efficient in sub-fs regime (the laser bandwidth must be at least of the order of the hydrogen ionization potential). We also showed that nondipole (retardation) effects play a crucial role over a large frequency range, i.e., from a few hundred eV to the keV regime. Although a considerable activity is devoted to shorten the FEL pulse duration below the fs (see [24–26] for recent works), the FELs usually operate in fs regime.

We note a recent calculation of Simonsen and Førre [27] which refers to dipole-forbidden atomic transitions induced by ultra intense x-ray laser fields. They solve the time-dependent Schrödinger equation (TDSE) for a hydrogen atom, initially prepared in the $2s$ and/or $2p(m = \pm 1)$ states, irradiated by 0.8 keV photons in pulses of 1–250 fs duration and intensities in the range $10^{20–23}$ W cm$^{-2}$ (much higher than the intensity considered in the present work). They show that the beyond-dipole two-photon Raman-like transition between the $2s$ and $2p(m = \pm 1)$ states completely dominates the underlying laser–matter interaction.

In this paper we explore SRS due to a pulse in the case of the hydrogen atom in an initial $2s$ state. As we will see below, we are in more favorable experimental conditions regarding the pulse duration since it is now in the fs domain. The two-photon SRS process populates the $1s$ state (anti-Stokes) as well as $nl$ states with $n > 2$ (Stokes). Furthermore, the study of SRS from orbitals different from $1s$ is interesting in view of future investigations with complex atomic systems.

In the above mentioned study of SRS in H(1s) [23], we have derived a formula valid in second-order perturbation theory (PT) for the case of a classical electromagnetic field modeled by a radiation pulse of finite duration. This formula (see equation (19) of [23]) expresses the transition amplitude as an integral over the pulse spectrum of the KHW (in reference to the works of Kramers, Heisenberg [28] and Waller [29]) matrix element multiplied by two values of the Fourier transform of the field vector potential. We used that formula for the study of SRS from the ground state of hydrogen. It can be written for any initial and final bound states and we use it in the present work, as expressed in equation (17) below, for the case of $2s$ initial state. More than this, we have shown that an approximation of the integral, in which the KHW matrix element for a pair of frequencies close to the central frequency of the pulse is factored out, works very well. Now, we calculate the probabilities of Raman transitions from the metastable $2s$ state of hydrogen to final $np$, $ns$ and $nd$ states, due to the interaction with an electromagnetic radiation pulse, the central photon frequency ranging from 5 to 55 au, with an intensity of $I_0 = 3.51 \times 10^{16}$ W cm$^{-2}$ corresponding to an electric field of 1 au (at its maximum). This rather large intensity raises the question of the pertinence of PT, in particular for photon energies of a few hundred eV. In many cases the PT approach turns out to be more tractable than TDSE from the computational point of view, but one must check that these methods lead to similar results. Thus, results based on the integration of TDSE are compared with those obtained by applying PT.

The paper is organized as follows: section 2 refers to the theory, first we recall some references for theoretical studies of two-photon processes involving bound states of hydrogen. Then we describe the Hamiltonian and the vector potential $A$ attached to the electromagnetic pulse and we briefly recall the main steps of the TDSE integration. In the last part of section 2 we present the PT formula used in the present work. For $ns$ and $nd$ transitions we adopt the dipole approximation (DA) connected with the $A \cdot \mathbf{P}$ term in the Hamiltonian, for $np$ transitions we use the first-order correction due to retardation in the $A^\mathbf{r}$ term. In contrast with our previous studies of H(1s) SRS, in which we used analytic expressions for the KH (in reference to the work of Kramers and Heisenberg [28]) matrix element as given in [30], we calculate for the case of H(2s) SRS this matrix element in two different ways, (i) using analytic expressions presented in appendix A.1 and (ii) applying the numerical procedure
described in appendix A.2. Results are given in section 3 and the conclusions are presented in section 4.

2. Theory

2.1. Perturbation theory for two-photon transitions in hydrogen induced by monochromatic plane waves

In this subsection we refer to results based on the description of multiphoton processes in perturbation theory and with radiation sources modeled by monochromatic plane waves.

The first approach of two-photon transitions involving atomic bound states, due to Kramers and Heisenberg [28], concerns radiation scattering, elastic (Rayleigh) or inelastic (Raman) and was based on the correspondence principle. The differential cross section of the process was expressed in terms of a matrix element derived first in DA, the KH matrix element (given in equation (A.3)), the retardation effect was included later by Waller [29]. Goeppert-Mayer [3] derived not only the formula for the two-photon decay rate from the 2s state but also for its excitation from the ground state by simultaneous absorption of two photons. Kramers and Heisenberg formula, as well as the Goeppert-Mayer one, are expressed in terms of an infinite sum of terms covering the whole energy spectrum of the atom (discrete and continuum).

Since the seminal work of Goeppert-Mayer other calculations on bound–bound two-photon processes have been performed. A new direction in the study of bound–bound transitions flourished around the year 1968, when it was found that the KH matrix elements for lowest bound states of hydrogen can be expressed by simple analytic formula. An account of the results obtained using the Coulomb Green’s function, some worked in parallel and independently by physicists from different countries, can be found in the review paper of Maquet, Véniard and Marian [31]. The closed-form analytic expressions of the transition amplitudes made the numerical predictions more accessible than the other existing techniques. We mention explicitly here Gavrila’s result for 1s Rayleigh scattering amplitude [32] for its intrinsic value and particularly because it opens the path to an area of research that was followed at the University of Bucharest by a team of young physicists, among whom were two of the authors of the present paper (VF and TM).

The 2s state interaction with the electromagnetic interaction was studied by Klarfeld [33] who gave analytic expressions for the cross sections of anti-Stokes Raman scattering 2s–1s, stimulated two-photon emission and Rayleigh scattering. Klarfeld also published values of these cross sections for wavelengths ranging from 5000 to 10000 Å. Independent calculations have been done by Zon, Manakov and Rapoport [34]. Later, Heno et al [35] have included calculations for the cross sections for 2s–3s and 2s–3d Raman transitions.

The very compact analytic expressions for the two-photon bound–bound matrix element for hydrogen obtained by Marian [36] refer to any pair of bound states \((nl \rightarrow nl')\) with \(l' = l, l \pm 2\) and have the advantage that they can be used for any bound–bound two-photon process (two-photon absorption or emission from the lowest or highest state, respectively, Rayleigh scattering on a given bound state, Raman Stokes or Raman anti-Stokes scattering transitions).

The main elementary inelastic process underlying light scattering using a monochromatic source of low intensity is the absorption of one photon from the source simultaneously with the spontaneous emission of another photon, of different energy. In Raman scattering from the ground state of hydrogen, the final state of the atom is an excited state. The results of calculations are expressed in terms of cross sections [33–35]. For our further purposes, we write the differential cross section for the Raman type transition from the 2s state to a bound state \(b\).

\[
\frac{d\sigma_{\text{Raman}}}{d\Omega_2} = \frac{\omega_2}{\omega_1} |\mathcal{M}_{b,2s}^{\text{KHW}}(\omega_1, \omega_2)|^2,\]

with \(n_0\) the classical radius of the electron and \(\mathcal{M}_{b,2s}^{\text{KHW}}\) the KHW matrix element (A.1). \(\omega_1\) is the frequency absorbed from the source and \(\omega_2\) is the spontaneously emitted frequency. Energy conservation requires

\[
E_{2s} + \hbar\omega_1 = E_b + \hbar\omega_2.
\]

The direction and polarization of the emitted photon are not fixed. Anti-Stokes Raman scattering, in which the metastable 2s state decays, is described by the same equation as above with \(b\) replaced by 1s. In this case the emitted frequency \(\omega_2\) is larger than the absorbed one. The existing numerical calculations [33–35] of the anti-Stokes Raman cross sections correspond to low-frequency regime (visible and UV).

In the presence of a second source of frequency \(\omega_2\) Raman scattering is stimulated, the emission of a photon having the characteristics of the second photon source is favored. The connection between the rates for SRS and Raman scattering reads

\[
\Gamma^{\text{SRS}} = \frac{8\pi\lambda^2}{\hbar\omega_2^3} \frac{21}{212} \frac{d\Gamma_{\text{Raman}}}{d\omega_2} d\Omega_2.
\]

On the right side one finds the value of \(d\Gamma_{\text{Raman}}/(d\omega_2 d\Omega_2)\) attached to the frequency, direction of propagation and polarization of the second source of intensity \(I_2\) whose presence stimulates the emission. This is the analogous of equation (15) of [37] valid for stimulated Compton scattering. The cross section of SRS is

\[
\sigma^{\text{SRS}} = \frac{8\pi\lambda^2}{\hbar\omega_2} \frac{21}{212} \frac{d\sigma_{\text{Raman}}}{d\Omega_2} \delta(\omega_2 - \omega_1 - \omega_{2s,1}).
\]

In the PT calculations developed here for SRS, the two monochromatic sources are replaced by one pulse with the central frequency \(\omega_1 \approx 5–55\) au and a bandwidth allowing SRS excitation (for fs and sub-fs pulses) and stimulated anti-Stokes 2s–1s transition (for sub-fs pulses). Below we shall see that the KHW matrix element (A.1) plays a key role also in the case of the Raman scattering of a radiation pulse, see equations (16) and (17).

2.2. General equations

The nonrelativistic Hamiltonian representing the electron in the Coulomb field of the nucleus, in interaction with an
electromagnetic field of vector potential $\mathbf{A}$, is written (in the Coulomb gauge)
\begin{equation}
\mathcal{H} = \frac{1}{2m_e} \mathbf{P}^2 - \frac{e^2}{4\pi\varepsilon_0 r} - \frac{e}{m_e} \mathbf{A} \cdot \mathbf{P} + \frac{e^2}{2m_e} \mathbf{A}^2, \quad \nabla \cdot \mathbf{A} = 0,
\end{equation}
where $e < 0$ and $m_e$ are the electron charge and mass, respectively, in SI units. The vector potential $\mathbf{A}$ describes a radiation pulse linearly aligned along the $z$ axis (unity vector $\mathbf{e}_z$) and propagating along a direction $\mathbf{n}$ in the $xy$ plane:
\begin{equation}
\mathbf{A} = A(t')\mathbf{e}_z, \quad t' = t - \mathbf{n} \cdot \mathbf{r}/c, \quad A(t') = A_0 f(t'),
\end{equation}
where $A_0$ is its peak value and $f(t')$ its carrier multiplied by a slowly varying envelope. For numerical simulations, as in our precedent works, $A(t)$ is non-zero over a time interval $(-\tau/2, \tau/2)$ where $\tau$ is the total pulse duration, and it is chosen to have a cos$^2$ envelope.

The spectral properties of the pulse are characterized by the Fourier transform $\varphi(\omega)$ of the function $f(t)$,
\begin{equation}
\varphi(\omega) = \int f(t)e^{i\omega t} dt, \quad f(t) = \frac{1}{2\pi} \int \varphi(\omega)e^{-i\omega t} d\omega.
\end{equation}
The function $|\varphi(\omega)|$ reaches its maximum value for $\omega = \pm \omega_0$, where $\omega_0$ is the central frequency of the pulse. The spectral width $\Delta \omega$ of the pulse, defined as the full width at half maximum of $|\varphi(\omega)|^2$, is given in the case of a cos$^2$ pulse by $\Delta \omega \approx 1.44\omega_0/N$, where $N$ is the number of carrier cycles.

As we shall see in section 2.4 the function
\begin{equation}
\Phi(\bar{\omega}, \omega) \equiv \varphi(\omega)\varphi(\bar{\omega} - \omega) = \varphi(\omega)\varphi(\omega - \bar{\omega}),
\end{equation}
where the parameter $\bar{\omega}$ holds for the Bohr frequencies relevant to the studied transitions, plays an important role in the main equations used in PT (where the temporal shape of the pulse is taken into account). If the pulse duration is very long, the pulse becomes quasi-monochromatic and the function $\Phi$ takes negligible values due to the fact that the laser bandwidth $\Delta \omega$ goes to zero as the pulse duration increases to infinity.

2.3. The integration of the TDSE, basis equations

For the numerical integration of the TDSE, we adopt an approximate form of the vector potential in the Hamiltonian [38]; with the choice of $x$ axis taken along the pulse propagation direction $\mathbf{n}$, $A(t')$ is given in first approximation by
\begin{equation}
A(t') \approx A(t) + F(t)\chi/c,
\end{equation}
where $F(t)$ is the electric field in DA, and the Hamiltonian is approximated by
\begin{equation}
\mathcal{H} \approx \mathcal{H}_e + \mathcal{H}_{DA}^{(1)} + \mathcal{H}_{RET}^{(1)} + \mathcal{H}_{RET}^{(2)}.
\end{equation}
This approximate Hamiltonian is written as a sum of the atomic Hamiltonian $\mathcal{H}_e \equiv \mathbf{P}^2/2m_e - e^2/4\pi\varepsilon_0 r$, of the interaction term in DA, $\mathcal{H}_{DA}^{(1)} \equiv -(e/m_e)A(t)P_z$, and of other two terms, describing nondipole corrections: $\mathcal{H}_{RET}^{(1)} \equiv -(e/m_e) F(t) x P_z$ and $\mathcal{H}_{RET}^{(2)} \equiv (e^2/m_e) F(t) A(t)x$. We note that we neglected the terms of higher order in $1/c$—a procedure justified in the nonrelativistic theory—which is the present case. At the same time we remark that the interaction terms have a very simple structure (a time-dependent function multiplied by a time-independent electron operator), which is very convenient for numerical calculations. Different selection rules are associated with the three interaction terms, namely ($l'= l \pm 1; m' = m$) for $\mathcal{H}_{DA}^{(1)}$, ($l'= l, l \pm 2; m' = m \pm 1$) for $\mathcal{H}_{RET}^{(1)}$, and ($l'= l \pm 1; m' = m \pm 1$) for $\mathcal{H}_{RET}^{(2)}$.

For the numerical integration of the TDSE with the Hamiltonian (10), we have used a spectral method based on the expansion of the wave function
\begin{equation}
\psi(\mathbf{r}, t) = \sum_{n,l,m} e^{-iE_{nlm}(t)} c_{nlm}(t) u_{nlm}(\mathbf{r})
\end{equation}
in a discrete basis of the atomic Hamiltonian $\mathcal{H}_e$. We use six angular momenta $l = 0$–$5$, with $|m| \leq l$, and a radial basis of 2400 B-spline functions of order $k = 7$, distributed linearly inside a box of length $R = 600$ au. We have checked that the population of the states with $l > 2$ is negligible, the numerical convergence of the calculations has been also checked by changing the box size and/or the number of B-splines—for details see the papers [39, 40]. The coupled differential equations satisfied by the coefficients $c_{nlm}(t)$ are integrated over the pulse duration using a Runge–Kutta method, with initial conditions corresponding to the atom in the excited state $2s$. The total CPU time is of the order of 10–20 h, depending on the laser parameters, and parallel computing is used. The populations of the bound states at the end of the pulse are simply calculated taking the squared moduli of the coefficients in equation (11) at $t = \tau/2$.

2.4. Perturbation theory applied to the interaction with an electromagnetic pulse

In our recent paper [23], using the time-dependent PT applied to the Hamiltonian (5), we have expressed the Raman transition amplitude from the ground state (see equation (15) from [23]), treating the terms $A(t')A(t'P_z$ in first and second-order of PT, respectively. A similar equation is valid for any bound–bound transitions, and we reproduce it here using the indices suited for a transition from the $2s$ state to another bound state $b$,
\begin{equation}
A_{2s\rightarrow b} = \frac{1}{2\pi\hbar} \frac{(eA_0)^3}{m_e} \int d\omega \varphi(\omega)\varphi(\omega_{b,2s} - \omega) T_{b,2s}(\omega),
\end{equation}
where the integral with respect to $\omega$ is on the real axis and
\begin{equation}
T_{b,2s}(\omega) \equiv \frac{1}{2} \left\langle \hat{h}|e^{i\omega_{b,2s} - \omega}\hat{P}_z G^{(+)}(E_{2s} + \hbar\omega)e^{i\omega}\hat{P}_z|2s\right\rangle.
\end{equation}
The function $\varphi(\omega)$ is the Fourier transform of the vector potential scaled to its peak value, $A(t)/A_0$, defined in equation (7). We note that the Bohr frequency $\omega_{b,2s} = (E_b - E_{2s})/\hbar$ can be negative or positive. Proceeding like in [23], particularly using
the relation
\[ \mathcal{J}_{b,2}(\omega) + \mathcal{J}_{h,2}(\omega_{b,2} - \omega) \equiv \mathcal{M}_{b,2}^{KH}(\omega, \omega - \omega_{b,2}), \] (14)
with \( \mathcal{M}_{b,2}^{KH} \) the KHW matrix element (A.1), we reach a final expression for the transition amplitude, corresponding to the equations (19) and (20) in [23],
\[ A_{2s\rightarrow b} = \frac{1}{2\pi \hbar} \frac{(eA_{0})^2}{m_e} \mathcal{J}_{b,2s}, \] (15)
\[ \mathcal{J}_{b,2s} = \int_{\omega_{b,2s}}^{\infty} d\omega\ \Phi(\omega_{b,2s}, \omega) \mathcal{M}_{b,2}^{KH}(\omega, \omega - \omega_{b,2s}), \] (16)
where the function \( \Phi(\omega_{b,2s}, \omega) \) is defined in equation (8). We note that the low frequency contribution to the integral (16), including the region \( \omega < 0 \) in the case \( b = 1s \), is negligible here (see below). For the probability of the SRS process we get
\[ p_{2s\rightarrow b} = \left| A_{2s\rightarrow b} \right|^2 = \frac{(eA_{0})^4}{4\pi^2 \hbar^2 m_e^2} \left| \mathcal{J}_{b,2s} \right|^2 = 16 \alpha^2 \frac{I^2}{m_e^2 \omega_0^2} \left| \mathcal{J}_{b,2s} \right|^2, \] (17)
where \( I \) is the intensity corresponding to the peak value of the electric field, \( F_0 = \omega_0 A_0 \).

As remarked in [23], in the case of a pulse we meet the KHW matrix element \( \mathcal{M}_{b,2}^{KH}(\omega, \omega - \omega_{b,2s}) \) of SRS in the presence of two fictitious monochromatic fields with frequencies \( \omega \) and \( \omega' \equiv \omega - \omega_{b,2s} \). The wave vectors of the two fields
\[ \mathbf{k} = \frac{\omega}{c} \mathbf{n}, \quad \mathbf{k}' = \frac{\omega'}{c} \mathbf{n}, \] (18)
are along the pulse direction \( \mathbf{n} \), their difference being \( \mathbf{k} - \mathbf{k}' = \omega_{b,2s} \mathbf{n}/c \).

An efficient approximation of the transition amplitude was obtained in [23] exploiting the spectral properties of the overlap function (8). We apply it to the transitions from 2s. The pulse enters in equation (16) only through the function \( \Phi(\omega_{b,2s}, \omega) \), whose properties are dictated by two parameters, the Bohr frequency \( \omega_{b,2s} \) and the pulse bandwidth \( \Delta \omega \). The overlap \( \Phi(\omega_{b,2s}, \omega) \) of the two Fourier transforms is large if \( \Delta \omega \) is comparable with \( |\omega_{b,2s}| \) or higher, and small in the opposite case, going to zero for the case of the monochromatic field. We denote by \( \mathcal{I} \) a frequency interval including \( (\omega_0, \omega_0 + \omega_{b,2s}) \) (the bounds have to be interchanged if \( b \equiv 1s \)) where the function \( \Phi(\omega_{b,2s}, \omega) \) takes significant values, and giving the dominant contribution to the integral (16). We note that its width depends on the ratio \( \Delta \omega/|\omega_{b,2s}| \).

For the frequencies and pulse durations considered here, the variation of the matrix element \( \mathcal{M}_{b,2s}(\omega, \omega - \omega_{b,2s}) \) over the frequency interval \( \mathcal{I} \) can be neglected. Approximating it by its value at a frequency \( \omega_1 \) between \( \omega_0 \) and \( \omega_0 + \omega_{b,2s} \), the integral (16) reads
\[ \mathcal{J}_{b,2s} \approx \mathcal{K}(\omega_{b,2s}) \mathcal{M}_{b,2s}^{KH}(\omega_1, \omega_2), \] (19)
where \( \omega_2 \equiv \omega_1 - \omega_{b,2s} \) and with the notation
\[ \mathcal{K}(\bar{\omega}) \equiv \int_{\mathcal{I}} d\omega\ \Phi(\bar{\omega}, \omega) = \int_{\mathcal{I}} d\omega\ \varphi(\omega) \tilde{\varphi}(\bar{\omega} - \omega). \] (20)

Adopting the approximation described above, the final result for the transition amplitude is
\[ A_{2s\rightarrow b} \approx \frac{1}{2\pi \hbar} \frac{(eA_{0})^2}{m_e} \mathcal{K}(\omega_{b,2s}) \mathcal{M}_{b,2s}^{KH}(\omega_1, \omega_2). \] (21)
the corresponding transition probability being
\[ p_{2s\rightarrow b} \approx 16 \alpha^2 \frac{I^2}{m_e^2 \omega_0^2} \left| \mathcal{J}_{b,2s} \right|^2. \] (22)

The last formula displays a separation of the spectral properties of the pulse, manifested only in the integral \( \mathcal{K} \), from those of the atom, entering in the matrix element \( \mathcal{M}_{b,2s}^{KH} \) and in \( \mathcal{K} \) through the Bohr frequency \( \omega_{b,2s} \). The optimal choice of \( \omega_1 \) is in the middle of the interval in between \( \omega_0 \) and \( \omega_0 + \omega_{b,2s} \). Thus, we have
\[ \omega_1 = \omega_0 + \omega_{b,2s}/2, \quad \omega_2 = \omega_0 - \omega_{b,2s}/2. \] (23)

As explained in [23], this choice is in favor of the approximation (21) in the case of a function \( \Phi(\omega_{b,2s}, \omega) \) symmetric around \( \omega_1 \). This situation arises in particular if the pulse has a shape described by an even function of time.

For the numerical calculation of the amplitude (16) we used the approximation for the matrix element \( \mathcal{M}_{b,2s}^{KH} \) described by equation (A.2) and previously so-called [23] ‘hybrid’ approximation. Consequently, the amplitude (16) is the sum of two terms
\[ \mathcal{J}_{b,2s} = \mathcal{J}_{b,2s}^{DA} + \mathcal{J}_{b,2s}^{RE}, \] (24)
with
\[ \mathcal{J}_{b,2s}^{DA} = \int_{\omega_{b,2s}/2}^{\infty} d\omega\ \Phi(\omega_{b,2s}, \omega) \mathcal{M}_{b,2s}^{KH}(\omega, \omega - \omega_{b,2s}), \] (25)
and
\[ \mathcal{J}_{b,2s}^{RE} = \frac{i}{c} \omega_{b,2s} (\mathbf{n} \cdot \mathbf{r}_{b,2s}) \int_{\omega_{b,2s}/2}^{\infty} d\omega\ \Phi(\omega_{b,2s}, \omega). \] (26)

We note that the first term in equation (A.2), leading to (25), is responsible for the Raman transitions to the \( ns \) and \( nd \) states, while the last term (related to retardation effects) leads to transitions to \( np \) states. The separation of the contributions associated with the coupling terms \( \mathbf{A} \cdot \mathbf{P} \) and \( \mathbf{A}' \) in the transition probabilities (no interference terms) is due to the fact that the selection rules in equations (25) and (26) involve different angular channels (see section 2.3). The probability of the SRS process is then
\[ p_{2s\rightarrow b} = p_{2s\rightarrow b}^{DA} + p_{2s\rightarrow b}^{RE}, \] (27)
with
\[ p_{2s\rightarrow b}^{DA} = 16 \alpha^2 \frac{I^2}{m_e^2 \omega_0^2} \left| \mathcal{J}_{b,2s}^{DA} \right|^2 \] (28)
and
\[ p_{2s\rightarrow b}^{RE} = 16 \alpha^2 \frac{I^2}{m_e^2 \omega_0^2} \left| \mathcal{J}_{b,2s}^{RE} \right|^2. \] (29)
where $b$ is $ns$ or $nd$ in (28) and $np$ in (29). For future reference we also transcribe equation (22) in DA

$$P^\text{DA}_{2s \rightarrow b} \approx 16 \alpha^2 \frac{I^2}{m_e \omega_0} |K(\omega_{b,2s})|^2 |\lambda_{b,2s}^{\text{KH}}(\omega_1, \omega_2)|^2. \quad (30)$$

3. Results and discussion

We present results for bound–bound Raman transitions from the $2s$ state, induced by a radiation pulse with a peak intensity fixed at $I_0 = 3.51 \times 10^{16}$ W cm$^{-2}$ for the frequency range extending from 5 to 55 au.

In figures 1–6 we present our numerical results for Raman transition probabilities, obtained by two different methods: integration of TDSE and lowest-order perturbation theory (LOPT). For LOPT we use equation (30) which neglects the variation of the KH matrix element $\mathcal{M}$ under the integral (25) with the frequency, and the equation (29). LOPT results calculated with equation (28), where the corresponding integral (25) is evaluated without approximating $\mathcal{M}$, are included in figure 5. The KH matrix element $\mathcal{M}$ is calculated for the $2s$–$ns$ and $2s$–$nd$ transitions with the analytic expressions given in appendix A.1 or using the numerical approach developed in appendix A.2.

For the first four figures the calculations are performed for a pulse of fixed duration $\tau = 6\pi$ au (about 0.45 fs), in this case the spectral width ($\Delta \omega = 0.48$ au) is larger than the Bohr frequencies corresponding to any pair of states ($b \equiv nl$, 2s).

In figure 1 we only show TDSE results. The quantity represented is the total transition probability versus the pulse frequency for $\omega_0 = 5$–55 au. The total probability is approximated by the sum over the $ns$ contributions (for $n = 1$–13, the contribution of 2s state being excluded) and over $p$ and $d$ channels up to $13p$ and $13d$, respectively. The

Figure 1. Total transition probability for a pulse with peak intensity $I = I_0 = 3.51 \times 10^{16}$ W cm$^{-2}$ and a total duration of $\tau = 6\pi$ au (≈ 0.45 fs). The calculations, based on TDSE, are performed: in DA for the $A^2$ term (AP), considering only the term $\mathcal{H}^{(2)}_\text{RET}$ originating from $A^2$ (see equation (10)) ($A^2$) and with the full Hamiltonian (FH). The figure also shows the total of $A^2$ and AP contributions.

Figure 2. Partial and total transition probabilities for $nl$ states for the same pulse as in figure 1. TDSE calculations are performed with the full Hamiltonian.

Figure 3. Partial and total transition probabilities for $ns$ and $nd$ states calculated in LOPT (lines) and resolving the TDSE (symbols). All calculations are performed within the DA.

Figure 4. Partial and total transitions probabilities for $np$ states calculated in LOPT (lines) and resolving the TDSE (symbols). All calculations are based on the interaction term $\mathcal{H}^{(2)}_\text{RET}$ originating from $A^2$ (see equation (10)).

TDSE results are obtained: (i) in DA (labeled ‘AP’ in the figure), (ii) keeping only the interaction term $\mathcal{H}^{(2)}_\text{RET}$ originating from $A^2$ term (label ‘$A^2$’), (iii) with the full Hamiltonian (10) (‘FH’), and (iv) taking the sum of (i) and (ii) (label ‘$A^2$+AP’). The comparison between FH and AP (in DA) results shows that the retardation effects are important in the higher part of the frequency range, for $\omega_0 > 20$ au and
The retardation effect is much faster than the ND one when the frequency increases.

Figure 5. Transition probabilities for ns states calculated resolving the TDSE (circle symbol) and in LOPT: with lines results obtained using equation (30), with symbols (other than circles) results calculated with equation (28). The corresponding LOPT total probabilities are labeled by 'Tp30' and 'Tp28'. Calculations are performed in DA.

Figure 6. Same as figure 5, for np states. Calculations are based on the interaction term $\mathcal{H}^{\text{RET}}_{\text{nondipole}}$ originating from $A^2$ (see equation (10)).

The retardation effect is mainly due to the term associated with $A^2$, a feature directly confirmed by comparing the $A^2$ and FH calculations in figure 1.

In figure 2 we present the results with full Hamiltonian in more detail, showing the transition probabilities to ns, np and nd states, and keeping only the nl states with the largest populations. We do not show the populations of the 2p states, in fact they are extremely small. This is in agreement with LOPT which predicts that the contributions of $A \cdot P$ (DA) and $A^2$ terms to the 2s–2p transition are both equal to zero. Comparing the relative contribution of the states we remark that the nd states have a modest contribution relatively to ns states over the whole interval considered. Here we recall that the ns and nd states are populated through the retardation term $\mathcal{H}^{\text{RET}}_{\text{np}}$ (see equation (10)) associated with $A \cdot P$. We have checked that the retardation terms play a minor role in the case of the dominant contributions ns, but the nondipole correction term $\mathcal{H}^{\text{nondipole}}_{\text{nondipole}}$ (see equation (10)) associated with $A \cdot P$ has a non-negligible role in the population of nd states. The latter feature has been already noticed in [22]. In all other cases the $\mathcal{H}^{\text{nondipole}}_{\text{nondipole}}$ term plays a minor role. The np states are populated through the retardation term $\mathcal{H}^{\text{RET}}_{\text{np}}$ associated with $A^2$. They dominate over the 1s contribution for frequencies larger than 20 au but we notice that, for $\omega_0 > 10$ au, the np populations already dominate over the 3s and 4s ones. The figure also shows that the ns transition probability decreases much faster than the np one when the frequency increases.

In figures 3 and 4 we compare the TDSE results with LOPT ones. As in the precedent case we only show the dominant nl populations. In figure 3 the ns and nd populations are calculated in DA, using equation (30). For the whole range considered we see a good agreement between the TDSE and LOPT approaches, confirming the validity of PT in our conditions. Note that, as seen in figure 1, for photon energies above 20 au the DA contributions (ns and nd states) are negligible compared to the $A^2$ (nondipole) ones (np states), a feature confirmed by the results in figures 3 and 4. Figure 4 shows the np populations calculated with the retardation term $\mathcal{H}^{\text{RET}}_{\text{np}}$ originating from $A^2$ (see equation (10)), using equation (29). The agreement between the LOPT and TDSE approaches is very good.

In figures 5 and 6 we examine, for a fixed central frequency $\omega_0$ of the pulse, the dependence on pulse duration $\tau$ of the transition probabilities. The value chosen for the central frequency, $\omega_0 = 15$ au, is in the intermediate frequency region where the contributions of the terms $A \cdot P$ and $A^2$ are comparable (in other words the ns and np channels have probabilities of the same order of magnitude, see figure 2). In figure 5 we present results for transitions due to the interaction term $A \cdot P$ in DA. The transition probability to ns states ($n = 2$) is calculated in LOPT in two ways: using equation (28) and its approximate version (30). The agreement of the two sets of LOPT results confirms the validity of the approximation leading to equation (22). The total probability for $n \leq 13$ is compared with the same quantity extracted from TDSE calculations. We remark that the transition probability to each ns state as function of $\tau$ has a maximum, whose position is n-dependent. The maximum for 1s appears around 18 au (about 0.43 fs) and is well separated from the other maxima, the significant ones being located in the region with $\tau > 50$ au ($\tau > 1.2$ fs). Consequently, the total probability has two maxima at about 20 and 85 au (about 2 fs), slightly closer than the peaks of the 1s and 3s dominant contributions. This double peak structure has a simple explanation, for long (fs) pulses the laser bandwidth is smaller than the 2s–1s energy separation and the anti-Stokes Raman process populating 1s is energetically quasi-forbidden. On the other hand, for short (sub-fs) pulses the bandwidth is larger and the latter process populates the 1s state but SRS is less efficient to populate the upper states, due to the low energy spectral density. Figure 6 shows results characterizing the contribution of the term $A^2$, in LOPT for transitions 2s–np ($n = 3–6$) and total transition probability for $n = 3–13$, the last one being compared with the same quantity calculated with TDSE. The dependence on the pulse duration for each $n$ is similar with the case previously discussed (figure 5), with the difference that the total probability shows a single maximum close to 90 au (about 2.17 fs), the 1s contribution being absent. Finally, we notice in figures 5 and 6 the very good agreement between...
LOPT and TDSE calculation for the total probabilities. We have checked that this agreement also holds for partial (nl) probabilities.

4. Conclusions

We have investigated bound-to-bound transitions in H(2s) by SRS of a pulse of intensity of $3.51 \times 10^{16}$ W cm$^{-2}$ in the xuv and soft x-ray domains and for fs and sub-fs pulse durations. We use TDSE and PT approaches, the Hamiltonian is treated in the nonrelativistic approximation and nondipole terms are included up to the order $1/c$.

First, comparing DA and nondipole numerical results for the total transition probabilities, we find that the nondipole term $\mathcal{A}^2$ plays a dominant role for pulse central frequencies larger than 20 au. Regarding the contribution of the $ns$, $nd$ (populated through $\mathbf{A} \cdot \mathbf{P}$) and $np$ (due to the nondipole term $\mathcal{A}^2$) series of states, we find that the $nd$ states have minor contributions for all cases investigated. Below the frequency of 15 au the contribution of $1s$ dominates. Here it must be noticed that the results on the frequency dependence in figures 1–4 have been obtained for a pulse duration of $6\pi$ (about 0.45 fs) corresponding to a laser bandwidth of the order of the ionization potential of the hydrogen atom. For larger pulse durations (corresponding to laser bandwidths smaller than the 2s–1s energy separation) the contribution of $1s$ becomes negligible. The $3p$ and $4p$ contributions overcome those of $3s$ and $4s$ for pulse frequencies larger than 10 au (about 270 eV).

Then, in figures 5 and 6 we have considered the case of a pulse frequency of 15 au, where the term $\mathbf{A} \cdot \mathbf{P}$ in DA (populating the $ns$ states and to a lesser extend the $nd$ states) and the correction term $\mathcal{A}^2$ (populating the $np$ states) have comparable contributions. The partial and total transition probabilities are calculated versus the pulse duration which is ranging from a few au to 250 au (about 6 fs). The calculations show that the total transition probabilities for $ns$ states have two maxima. The first one, at about 20 au (0.48 fs), originates from the contribution of $1s$, it quickly decreases for larger pulse durations. The second maximum, close to 85 au (about 2 fs), is due to $ns$ states (with $n > 2$). A similar feature is observed for $np$ states, with the difference that a single maximum is observed, since the $1s$ state is no longer populated. Finally, we have checked that TDSE results are in very good agreement with the PT calculations, confirming that LOPT applies in our case. This is of particular importance since PT calculations are much easier from the computational point of view. In agreement with PT, the populations vary quadratically with the intensity, nevertheless, increasing the intensity beyond the value used here ($3.51 \times 10^{16}$ W cm$^{-2}$), LOPT may loose its validity. For much higher intensities relativistic corrections of the order of $1/c^2$ (or higher) may also become non-negligible.

In conclusion, we have demonstrated that nondipole effects play a crucial role for SRS transitions from H(2s), for laser frequencies in the xuv domain and for femtosecond pulse durations. This should encourage the exploration of SRS of excited hydrogen or more complex atoms around FEL facilities. Also, owing to the large intensities now available at these facilities, it is of particular interest to explore relativistic effects in SRS and, more generally, in the context of nonlinear effects of Compton and Raman type.

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Appendix. The evaluation of the Raman scattering matrix element from the initial 2s state

In the Kramers–Heisenberg–Waller matrix element for Raman scattering from the 2s state to a bound state

$$
\mathcal{M}_{s,2s}^{\text{KHW}}(\omega, \omega') = \frac{1}{m_e} \langle b | e^{i \frac{\omega}{\hbar} \mathbf{r} \cdot \mathbf{P}} G^{(+)}(E_{2s} + \hbar \omega)e^{i \frac{\omega}{\hbar} \mathbf{r} \cdot \mathbf{P}} | 2s \rangle + \frac{1}{m_e} \langle b | e^{i \frac{\omega}{\hbar} \mathbf{r} \cdot \mathbf{P}} G^{(+)}(E_{2s} - \hbar \omega)e^{i \frac{\omega}{\hbar} \mathbf{r} \cdot \mathbf{P}} | 2s \rangle,
$$

(A1)

in which the two frequencies $\omega$ (absorbed) and $\omega'$ (emitted) are connected by $E_{2s} + \hbar \omega = E_{2s} + \hbar \omega'$, we consider the first two terms in DA and we only include the first nondipole correction in the last term (originating from the term $\mathcal{A}^2$ of the Hamiltonian). In this approximation the matrix element of Raman scattering becomes:

$$
\mathcal{M}_{s,2s}^{\text{bhy}}(\omega, \omega') \equiv \mathcal{M}_{s,2s}^{\text{KHW}}(\omega, \omega') + i \frac{\omega_{2s}}{c} \mathbf{n} \cdot \mathbf{r}_{b,2s}.
$$

(A2)

The first term in this equation is the Kramers–Heisenberg–Waller matrix element

$$
\mathcal{M}_{s,2s}^{\text{KHW}}(\omega, \omega') = \frac{1}{m_e} \langle b | P_i G^{(+)}(E_f + \hbar \omega)e^{i \frac{\omega}{\hbar} \mathbf{r} \cdot \mathbf{P}} | 2s \rangle + \frac{1}{m_e} \langle b | P_i G^{(+)}(E_f - \hbar \omega)e^{i \frac{\omega}{\hbar} \mathbf{r} \cdot \mathbf{P}} | 2s \rangle
$$

(A3)

and it induces the $2s$–$ns$ and $2s$–$nd$ transitions, while the last term determines the $2s$–$np$ two-photon processes.
The two terms of the KH matrix element (A.3) have the same structure and require the evaluation of the 33 components of the more general tensor

$$
\Pi^{DA, 2s}_{jk} = \langle j | P_i G^{(+)}(E_i + \hbar \omega) P_a | k \rangle, \quad k, j = 1, 2, 3,
$$
(A.4)

where \(G(z) = (z - H)^{-1}\) is the resolvent operator associated with \(H\) and \(G^{(+)}(W) = G(W + i\varepsilon)\).

In the following we describe the methods used for the numerical evaluation of \((A.4)\).

A.1. Analytic expressions for the Kramers–Heisenberg matrix element for the 2s–ns and 2s–nd transitions

The numerical evaluation of the KH matrix element can be done using analytic expressions derived from a general formula published for bound–bound two-photon matrix elements in DA [36]. For 2s–ns and 2s–nd transitions the KH matrix element reads

$$
\Pi^{DA, ns, 2s}_{jk} = \frac{1}{3} a_{n,2}(\tau) \delta_{jk},
$$
$$
\Pi^{DA, nd, 2s}_{jk} = \frac{2}{15} b_{n,2}(\tau) C_{m,jk}, \quad \tau = i \sqrt{-2 \Delta_{au}};
$$
(A.5)

with \(C_{m,jk}\) the coefficient of \(x_i x_j / r^2\) in the expansion of the spherical harmonics \(Y_{m,n}\) in terms of Cartesian coordinates; in particular, \(C_{0,0,0} = \sqrt{5}\).

The two invariants amplitudes \(a_{n,2}\) and \(b_{n,2}\) are combinations of the following six Appell functions:

$$
f_1 = F_1(2 - \tau, -(n - 1), n + 4, 3 - \tau; x_{n,2}, y_{n,2}),
$$
(A.6)

$$
f_2 = F_1(3 - \tau, -(n - 1), n + 4, 4 - \tau; x_{n,2}, y_{n,2}),
$$
(A.7)

$$
f_3 = F_1(3 - \tau, -(n - 2), n + 4, 4 - \tau; x_{n,2}, y_{n,2}),
$$
(A.8)

$$
f_4 = F_1(2 - \tau, -(n - 3), n + 2, 3 - \tau; x_{n,2}, y_{n,2}),
$$
(A.9)

$$
f_5 = F_1(3 - \tau, -(n - 3), n + 2, 4 - \tau; x_{n,2}, y_{n,2}),
$$
(A.10)

$$
f_6 = F_1(3 - \tau, -(n - 4), n + 2, 4 - \tau; x_{n,2}, y_{n,2}),
$$
(A.11)

namely,

$$
a_{n,2}(\tau) = \frac{C_0}{3} \sum_{j=1}^{6} \alpha_j f_j,
$$

$$
b_{n,2}(\tau) = -\sqrt{(n^2 - 1)(n^2 - 4)} C_0 \sum_{j=1}^{6} \beta_j f_j,
$$

$$
C_n = 2^n n \sqrt{2n(2 + \tau)(3 - \tau)(n + \tau)^{n+4}}
$$
(A.13)

with

$$
\alpha_j = (n + 1)(n + 2)(n - \tau)^2 \gamma_j, \quad j = 1, 2, 3,
$$

$$
\alpha_j = -(n - 1)(n - 2)(n + \tau)^2 \gamma_j, \quad j = 4, 5, 6,
$$
(A.14)

$$
\beta_j = (n - \tau)^2 \gamma_j, \quad j = 1, 2, 3
$$

$$
\beta_j = -(n + \tau)^2 \gamma_j, \quad j = 4, 5, 6
$$
(A.15)

$$
\gamma_1 = \gamma_4 = (2 + \tau)(3 - \tau)(n^2 - \tau^2),
$$

$$
\gamma_2 = \gamma_5 = -(2 + \tau)^2 (n - \tau)^2
$$

(A.16)

$$
\gamma_3 = 8n(n - 1)\tau^2,
$$

$$
\gamma_6 = 8n(n - 3)\tau^2.
$$
(A.17)

and

$$
x_{n,2} = \frac{2 - \tau n + \tau}{2 + \tau n - \tau}, \quad y_{n,2} = \frac{2 - \tau n - \tau}{2 + \tau n + \tau}.
$$
(A.18)

In the particular cases \(n = 1\) and \(n = 2\) the number of Appell functions involved reduces to two, respectively, three. They are in fact Gauss hypergeometric functions. Using a recurrence relation among them we obtain the simple results mentioned below.

*The 2s–1s transition.* The amplitude \(a(2s–1s)\) in (A.12) coincides with that of the amplitude \(a(\tau)|_{n=2}\) in equation (A4) of [23]. We reproduce it, with the notation (A.18),

$$
a_{1,2}(\tau) = \frac{2^{11/2}}{3^3} \left[ \frac{3\tau}{2 + \tau} - \frac{2 - 1 - 3}{3 - \tau} \right] F_1\left(1, 5, 4 - \tau; \frac{y_{2,2}}{y_{2,2} - 1}\right),
$$
(A.19)

*The 2s–2s transition.* When the final and initial state coincide, the two-photon transition amplitude describes Rayleigh scattering. The absorbed and emitted photon have the same frequency \(\omega\), but could have different directions. In the DA, the amplitude depends only on \(\omega\); for the 2s state the Rayleigh amplitude reads

$$
\mathcal{M}^R_{2s}(\omega) = 1 + \Pi^{DA}_{33}(E_{2s} + \hbar \omega) + \Pi^{DA}_{33}(E_{2s} - \hbar \omega).
$$
(A.20)

The first term comes from first-order perturbation theory for the \(A^1\) term, see the hybrid matrix element. An analytic expression for the Rayleigh scattering amplitude from the 2s state has been derived by many authors, but the most compact form has been obtained by Klarsfeld [33]. From equation (3) of the quoted paper and using our result for \(a_{22}\) from equation (A.12) one infers the following equality

$$
\mathcal{A}_K(\Omega) \equiv \frac{1}{2} + \Pi^{DA}_{33}(\Omega) = \frac{5(2 - \tau)}{2(2 + \tau)(3 - \tau)} \times \frac{2F_1(1, -2, -\tau, 4 - \tau; \gamma_{1,2})}{2F_1(1, -2, -\tau, 4 - \tau; \gamma_{1,2})},
$$
(A.21)

with \(\tau\) and \(y_{1,2}\) defined, respectively, in (A.5) and (A.18). It follows that the transition amplitude (A.20) is

$$
\mathcal{M}^K_{2s}(\omega) = \mathcal{A}_K(E_2 + \hbar \omega) + \mathcal{A}_K(E_2 - \hbar \omega).
$$
(A.22)

We used this expression as a check for our general code and also for a comparison with Gavrilov numerical results for Rayleigh on 2s [41].

The numerical evaluation of the Appell functions was done using their standard integral representation [42].

A.2. Inhomogeneous differential equation type method for the calculation of the Kramers–Heisenberg matrix element

The numerical calculation of the components of the tensor (A.4) can be reduced to the evaluation of radial integrals with integrands expressed with solutions of the inhomogeneous radial Schrödinger equation. The procedure used belongs to a class of methods described in the literature (see for example [43, 44], and references therein), based on the idea of...
transforming the problem of the action of the Green operator into the equivalent one of solving an inhomogeneous differential equation.

We describe in the following the procedure, referring to the component $\Pi_{\beta}^{DA} \equiv \Pi_{33}^{DA}$ for which, passing to the position representation, we have

$$\Pi_{\beta}^{DA} = \hbar^2 \int \int \nu_{\beta}^{\mu}(r) G^{(+)}(W; r, r') v_{\beta}(r') \, dr \, dr', \quad (A.23)$$

where $G^{(+)}(W; r, r')$ is the Green function and

$$v_{\beta}(r) \equiv \frac{\partial}{\partial z} u_{\beta}(r). \quad (A.24)$$

The function $v_{nlm}(r)$ corresponding to an eigenfunction $u_{nlm}(r) = \frac{1}{\sqrt{\rho}} \chi_{nlm}(r) Y_{nlm}(\theta, \phi)$ has the following expression

$$v_{nlm}(r) = b_{l+1,m} \xi_{nl}(r) Y_{l+1,m}(\theta, \phi) + b_{lm} \eta_{nl}(r) Y_{l,m}(\theta, \phi), \quad (A.25)$$

where

$$\xi_{nl}(r) = \frac{d\chi_{nl}(r)}{dr} - \frac{l + 1}{r} \chi_{nl}(r), \quad \eta_{nl}(r) = \frac{d\chi_{nl}(r)}{dr} + \frac{l}{r} \chi_{nl}(r) \quad (A.26)$$

and

$$b_{lm} = \sqrt{\frac{l^2 - m^2}{4l^2 - 1}} \quad (l > 0), \quad b_{00} = 0. \quad (A.27)$$

We write the expansion of the Green function in spherical harmonics in the form

$$G^{(+)}(W; r, r') = \frac{2m_e}{\hbar^2} \sum_{lm} b_{lm}^{(+)}(W; r, r') \times Y_{lm}(\theta, \phi) Y_{lm}^*(\theta', \phi'), \quad (A.28)$$

where the radial Green function $g_{l}^{(+)}(W; r, r')$ is solution of the non-homogeneous equation

$$\frac{d^2g_{l}}{dr^2} + \frac{2m_e}{\hbar^2} [W - V_{ef}(l, r)] g_{l} = \delta(r - r'), \quad (A.29)$$

Replacing in (A.23) the expansions (A.25) for the functions $v_{\beta}, v_{\gamma}$ and (A.28) for $G^{(+)}$, one finds the following selection rules: $\Pi_{\beta}^{DA, F', n', \alpha', l', m', \alpha''}$ is non-vanishing if $l' = l - 2, l + 2$ and $m' = m$. We write explicitly the expressions of the non-vanishing matrix elements $\Pi_{\beta}^{DA}$ in the three cases

$$\Pi_{\beta, l-2, m, \alpha''}^{DA} = 2m_e b_{l-1,m} b_{l,m} A_{\alpha''}, \quad (A.30)$$

$$\Pi_{\beta, l, m, \alpha''}^{DA} = 2m_e (b_{l,m}^{2} B_{\alpha''} + b_{l+1,m}^{2} C_{\alpha''}), \quad (A.31)$$

$$\Pi_{\beta, l+2, m, \alpha''}^{DA} = 2m_e b_{l+2,m} b_{l+1,m} D_{\alpha''}, \quad (A.32)$$

where $A, B, C$ and $D$ denote the following radial integrals

$$A_{\alpha''} = \int_{0}^{\infty} dr b_{l-1,m}^{2} g_{l}^{(+)}(W; r, r') \eta_{\alpha''}(r'), \quad (A.33)$$

$$B_{\alpha''} = \int_{0}^{\infty} dr \eta_{\alpha''}(r) g_{l}^{(+)}(W; r, r') \eta_{\alpha''}(r'), \quad (A.34)$$

$$C_{\alpha''} = \int_{0}^{\infty} dr b_{l,m}^{2} g_{l}^{(+)}(W; r, r') \xi_{\alpha''}(r'), \quad (A.35)$$

$$D_{\alpha''} = \int_{0}^{\infty} dr \eta_{\alpha''}(r) g_{l}^{(+)}(W; r, r') \xi_{\alpha''}(r'), \quad (A.36)$$

The integrals in $r'$ in equations (A.33)–(A.36) are of the same type. With the generic notation

$$\phi(W, r) \equiv \int_{0}^{\infty} dr g_{l}^{(+)}(W; r, r') f(r') \quad (A.37)$$

and using equation (A.29), it follows that the function $\phi$ is solution of the inhomogeneous radial Schrödinger equation

$$\frac{d^2\phi}{dr^2} + \frac{2m_e}{\hbar^2} [W - V_{ef}(l, r)] \phi = f(r). \quad (A.38)$$

We apply the equations (A.30)–(A.36) in the case of an initial s state, i.e., $l = 0$ and $m = 0$. The non-vanishing matrix elements are

$$\Pi_{\alpha''}^{DA, n, l, s} = 2m_e b_{20}^{2} C_{\alpha''}, \quad \Pi_{\alpha''}^{DA, n, d, s} = 2m_e b_{20} b_{10} D_{\alpha''}. \quad (A.39)$$

The radial integrals involved can be simply expressed as

$$C_{\alpha''} = \int_{0}^{\infty} dr b_{l,m}^{2} \xi_{\alpha''}(r') \phi(W, r), \quad (A.40)$$

$$D_{\alpha''} = \int_{0}^{\infty} dr \eta_{\alpha''}(r) \xi_{\alpha''}(r') \phi(W, r), \quad (A.41)$$

where the function

$$\phi(W, r) \equiv \int_{0}^{\infty} dr g_{l}^{(+)}(W; r, r') \xi_{\alpha''}(r') \quad (A.42)$$

is the regular solution of equation (A.38), with $l = 1$ and $f(r) = \xi_{\alpha''}(r)$. We recall that one can represent a general solution of the inhomogeneous equation as a sum of a particular solution and of a general solution of the homogeneous equation

$$\frac{d^2\chi}{dr^2} + \frac{2m_e}{\hbar^2} [W - V_{ef}(l, r)] \chi = 0. \quad (A.43)$$

We also note that equations (A.38) and (A.42) take the same approximate form close to $r = 0$ and in the asymptotic region $r \to \infty$.

The numerical calculation of the matrix elements (A.39) is reduced now to the problem of finding regular solutions of equation (A.38) and calculating the corresponding integrals (A.40). We note that the regularity conditions uniquely determine the regular solution of equation (A.38) for $W < 0$, while for
$W > 0$ a supplementary condition is needed—this comes from the limit $\varepsilon \to 0$ in $G(W + i\varepsilon)$ requiring the solution to behave at large distances as a divergent spherical wave. For the integration of equation (A.38) we have used the Runge–Kutta method for $W > 0$ and a matrix approach for $W < 0$, based on an expansion of the solution in a B-spline basis.

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