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LETTER TO THE EDITOR

Analytical total photo cross section for atoms

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Abstract. A quantum–classical approximation for the total photo cross section of many-electron atoms is derived in a time-dependent formulation. Exact commutator relations for the time-dependent dipole operator and a classical approximation for the propagator are used. Analytical expressions are derived for one- and two-electron atoms. We compare the results for hydrogen with the exact cross section and the high-energy approximation. For helium we show a comparison with experimental data and accurate numerical results.

The total photo cross section of an atom is a ground-state property. Nevertheless, it is not readily calculated. Here, we present an approach which uses exact commutator relations for the hydrogenic time-dependent dipole moment and a classical approximation for the propagator to arrive at an analytical approximation.

To keep the derivation transparent we will illustrate the approach explicitly for photo-absorption from the ground state of a one-electron system. The transcription for many-electron systems is straightforward under some conditions to be specified. Excited initial states can also be treated. After a general formulation the application for the two-electron system of helium will be discussed.

In the dipole approximation the total photo cross section for a one-electron atom with nuclear charge Z may be written as (Heller 1978)

$$\sigma(\omega) = \frac{2\pi\alpha}{\omega}\int_{-\infty}^{\infty} \mathrm{d}t\, \langle\Psi|D(0)^{\dagger}D(t)|\Psi\rangle \mathrm{e}^{\mathrm{i}\omega t} \tag{1}$$

with the time-dependent dipole operator

$$D(t) = \mathrm{e}^{-\mathrm{i}Ht} D_0 \mathrm{e}^{\mathrm{i}Ht}\,. \tag{2}$$

The frequency of the photon is $\omega = E_f - E_i$, Ψ is the initial (ground-state) wavefunction and α is the fine structure constant. The idea of the following treatment is to derive two effective Hamiltonians which govern the dynamics before and after the absorption. This is similar to molecular photodynamics where the different electronic surfaces provide initial- and final-state Hamiltonians (Heller 1978, Braun *et al* 1995). In the atomic case the only difference before and after the absorption is the angular momentum. To see this difference explicitly we separate the angular degrees of freedom in (1) algebraically by inserting a complete set $\sum |lm\rangle\langle lm|$ of spherical harmonics at the appropriate places. Recalling that the dipole moment is a vector operator and assuming, for simplicity, linear polarization along the z-axis all sums collapse to one term and we get

$$\langle\Psi|D(0)^{\dagger}D(t)|\Psi\rangle = \int_{0}^{\infty} \mathrm{d}r\, \psi^{*} d_0^{\dagger} \mathrm{e}^{-\mathrm{i}H_1 t} d_0 \mathrm{e}^{\mathrm{i}H_0 t}\psi \tag{3}$$

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where

$$\psi = \langle 00|r\Psi\rangle = 2\beta^{3/2} r \mathrm{e}^{-\beta r} \tag{4}$$

and $\mathrm{e}^{-\mathrm{i}H_l t} = \langle l0|\mathrm{e}^{-\mathrm{i}Ht}|l0\rangle$ with

$$H_l = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{Z}{r} + \frac{l(l+1)}{2r^2}. \tag{5}$$

To be slightly more general we have used a screened hydrogenic wavefunction with effective charge β. The pure hydrogenic case is obtained by setting $\beta = Z$. For reasons that will become clear in a moment we will use the acceleration form for the dipole moment

$$D_0 = \frac{Z}{\mathrm{i}\omega}\frac{1}{r^2}\cos\Theta \tag{6}$$

and therefore

$$d_0 = \langle 10|D_0|00\rangle = \frac{1}{\sqrt{3}}\frac{Z}{\mathrm{i}\omega}\frac{1}{r^2}. \tag{7}$$

In the form of (7) the dipole operator is proportional to the centrifugal potential in H_l and we may write

$$\begin{aligned}\sigma(\omega) &\equiv \frac{2\pi\alpha Z^2}{3\omega^3}\int_{-\infty}^{\infty} \mathrm{d}t\,\langle\psi|(H_1 - H_0)\mathrm{e}^{-\mathrm{i}H_1 t}(H_1 - H_0)\mathrm{e}^{\mathrm{i}H_0 t}|\psi\rangle \mathrm{e}^{\mathrm{i}\omega t}\\ &= \frac{2\pi\alpha Z^2}{3\omega}\int_{-\infty}^{\infty} \mathrm{d}t\,\langle\psi|\mathrm{e}^{-\mathrm{i}H_1 t}\mathrm{e}^{\mathrm{i}H_0 t}|\psi\rangle \mathrm{e}^{\mathrm{i}\omega t}.\end{aligned} \tag{8}$$

This identity is the main result of the present study and can easily be verified by differentiating the integrand of (8) twice with respect to time and using the fact that ψ is an eigenfunction of H_0.

The form of (8) is identical to the nuclear dynamics of photoabsorption in molecules under the Born–Oppenheimer and Condon approximation (Heller 1978, Braun *et al* 1995). The dynamical problem to be solved involves forward propagation of the state ψ until time t on the 'lower' potential surface which is characterized by H_0, followed by a backward propagation on the 'upper' surface with H_1. If we use for both propagations the same approximation we can hope that errors will partially cancel. Writing $H_1 = H_0 + \Delta_1$ the obvious approximation is the zeroth-order term of the Baker–Hausdorff expansion

$$\mathrm{e}^{-\mathrm{i}(H_0+\Delta_1)t}\mathrm{e}^{\mathrm{i}H_0 t} \approx \mathrm{e}^{-\mathrm{i}\Delta_1 t}. \tag{9}$$

This amounts to neglecting all commutators between H_0 and Δ_1 and is therefore essentially a (semi-)classical approximation which can also be derived in a slightly different spirit from an expansion in $\hbar$. The result is known in molecular physics as the reflection principle (Heller 1978).

With equations (8) and (9) we can finally write the total cross section as

$$\sigma(\omega) \approx \frac{2\pi\alpha Z^2}{3\omega}\int_{-\infty}^{+\infty} \mathrm{d}t\,\langle\psi|\mathrm{e}^{-\mathrm{i}\Delta_1 t}|\psi\rangle \mathrm{e}^{\mathrm{i}\omega t}. \tag{10}$$

We will call (10) the hybrid approximation. It is quantum mechanical as far as the initial state and the exactly calculated commutators between the dipole moment and the propagator are concerned. Only the 'difference' of the propagation with H_0 and H_1 is approximated classically (see equation (9)).

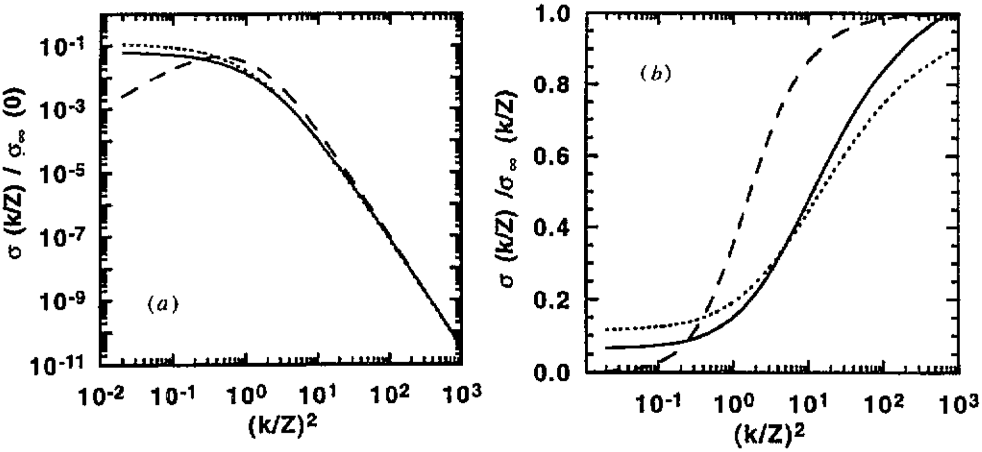

Figure 1. Total photoabsorption cross section for hydrogen: full curve, from (11), dotted curve, exact result; broken curve, high-energy approximation, the scaling function is $\sigma_\infty(y) = (\alpha\pi 2^8)/(3Z^2(y^2+1)^{3.5})$. (*a*) Logarithmic representation, (*b*) with the major energy dependence $\sigma_\infty(y)$ factored out.

The time integration in (10) leads now to a δ-function fixing the radial variable to $r = \omega^{-1/2}$. The final result with the wavefunction (4) is

$$\sigma_\beta(\omega) = \frac{Z^2}{\beta^4}\frac{2^7\pi^2\alpha}{3\sqrt{2}}\frac{1}{x^{7/2}}\mathrm{e}^{-\sqrt{8/x}} \tag{11}$$

where $x = 2\omega/\beta^2$. Note that the quantum–classical hybrid formulae (10) and (11) fulfil the sum rule for the oscillator strength. This is clear since the sum rule is the short-time limit and the only approximation was made in the time propagation.

In figure 1 the present result for hydrogen is compared to the exact cross section (Bethe and Salpeter 1977) and the usual high-energy approximation where the final state is replaced by a plane wave (Bethe and Salpeter 1977). Equation (11) is a reasonable approximation from threshold to several hundred eV and its superiority over the high-energy approximation is clearly seen. The hybrid formula has the correct high-energy dependence of $\omega^{-7/2}$ with a prefactor that is by 11% too large compared to the exact cross section. However, this will only have an effect well beyond 10^3 eV where Compton scattering will play an increasing role.

More importantly, the hybrid approach described can be applied to calculate total photo cross sections for many-electron systems with the Hamiltonian $H = H_0 + h$ where $H_0 = \sum_j H^{(j)}$ and $h = \sum_{j,k>j} V^{(jk)}$ with

$$H^{(j)} = -\tfrac{1}{2}\nabla_j^2 - \frac{Z}{r_j} \qquad V^{(jk)} = \frac{1}{|\boldsymbol{r}_j - \boldsymbol{r}_k|}\,. \tag{12}$$

In the spirit of the reflection principle the additional approximation of a classical propagation of the electron–electron interactions h is introduced. This is accomplished by using the first term of the Baker–Hausdorff formula in

$$\mathrm{e}^{\mathrm{i}(H_0+h)t} \approx \mathrm{e}^{\mathrm{i}H_0 t}\mathrm{e}^{\mathrm{i}ht} = \prod_j \mathrm{e}^{\mathrm{i}H^{(j)}t} \prod_{j,k>j} \mathrm{e}^{\mathrm{i}V^{(jk)}t}\,. \tag{13}$$

Under the approximation (13) we can write

$$\sigma(\omega) = \frac{2\pi\alpha}{\omega}\int_{-\infty}^{+\infty} \mathrm{d}t\,\langle\Psi|\mathcal{D}^{\dagger}(0)\mathcal{D}(t)|\Psi\rangle \mathrm{e}^{\mathrm{i}\omega t} \tag{14}$$

where the time-dependent dipole operator now has the form

$$\mathcal{D}(t) = \sum_j D^{(j)}(t) = \sum_j \mathrm{e}^{-\mathrm{i}H^{(j)}t} D_0^{(j)} \mathrm{e}^{\mathrm{i}H^{(j)}t}\,. \tag{15}$$

The interpretation of (14) is simple. The dipole operator for each electron j is propagated by the isolated dynamics of this electron only. However, electron–electron correlation has not been completely neglected in (14). Firstly, the interelectronic potentials are included classically and appear indirectly through the energy difference $\omega = E_f - E_i$. Secondly, there are 'cross'-terms between dipole operators of different electrons, $\langle\Psi|D^{(j)\dagger}(0)D^{(k)}(t)|\Psi\rangle$. These terms probe the electron correlation inherent in the initial-state wavefunction Ψ. The effect already becomes visible for a two-electron atom.

With a properly symmetrized ground-state wavefunction Ψ we may write

$$\sigma(\omega) = \frac{4\pi\alpha}{\omega}\int_{-\infty}^{+\infty} \mathrm{d}t\,(\langle\Psi|D^{(1)\dagger}(0)D^{(1)}(t)|\Psi\rangle + \langle\Psi|D^{(2)\dagger}(0)D^{(1)}(t)|\Psi\rangle)\mathrm{e}^{\mathrm{i}\omega t}\,. \tag{16}$$

The first term in (16) describes the one-electron contribution and the second term represents the correlation effect. It is absent for an uncorrelated initial state of the two electrons,

$$\Psi = \frac{\beta^3}{\pi}\mathrm{e}^{-\beta(r_1+r_2)} \tag{17}$$

under which the cross section simplifies considerably.

It can even be evaluated analytically with the reflection approximation (9) leading to the essentially hydrogenic result

$$\sigma(\omega) = 2\sigma_\beta(\omega) = \frac{Z^2}{\beta^4}\frac{2^8\pi^2\alpha}{3\sqrt{2}}\frac{1}{x^{7/2}}\mathrm{e}^{-\sqrt{8/x}} \tag{18}$$

where again $x = 2\omega/\beta^2$. For helium ($\beta = Z - \frac{5}{16}$, $Z = 2$) we compare in figure 2 the approximation (18) with the experiment by Samson *et al* (1994), and in figure 3 additionally with numerically converged data from Pont and Shakeshaft (1995). One sees immediately that the high-energy behaviour $\sigma \propto \omega^{-7/2}$ as derived by Bryon and Joachain (1967) is correctly reproduced. Below the double-ionization threshold (79 eV) resonances are interpolated smoothly by the hybrid formula (figures 2 and 3(*a*)). A closer inspection (figure 3(*b*)) shows that the values from (18) are slightly too low for moderate energies compared to the numerical and the experimental data. This finding is consistent with the one-electron case (figure 1) and is therefore not due to the more complicated two-electron dynamics. A slightly better agreement of the hybrid formula with the experiment and the numerical calculation is obtained if in the photon frequency $\omega = E - E_i$ the initial state energy is used, which is produced by the approximated wavefunction (17), namely $E_i = 2.848$ au (see figure 3).

The fact that photoabsorption in the two-electron system is well represented by the hybrid formula permits the conclusion that the physical picture behind the present approach is reasonable: initially *one* electron absorbs the photon and takes all its angular momentum and energy. This act is reflected in the total photo cross section which is sensitive mainly to short-time dynamics. Correlated many-electron dynamics develops subsequently and will

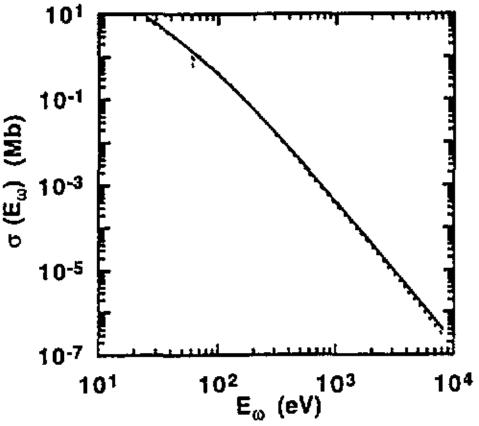

Figure 2. Total photoabsorption cross section for *helium: full curve, from (18) with initial energy* E_i = 2.848 au (see the text); broken curve, with experimental energy (indistinguishable from the full curve); dotted curve, experiment by Samson *et al* (1994).

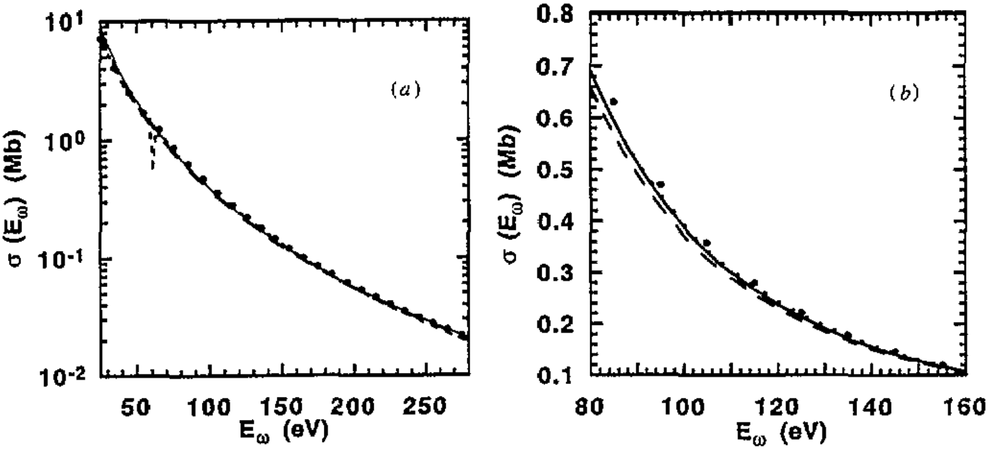

Figure 3. Same as figure 2 with additional full circles: numerical calculation by Pont and Shakeshaft (1995). (*a*) On a logarithmic scale, (*b*) on a linear scale.

lead to an exchange of energy and angular momentum between the electrons and in the case of helium eventually to some double-ionization events (Rost 1995). These long-time effects can, of course, not be described by the crude approximations (9) and (13) to the propagator.

In summary we have derived a simple quantum–classical hybrid approximation for photoabsorption in many-electron atoms. Based on this hybrid approach analytic formulae for the total photo cross section in one- and two-electron atoms have been given. From comparison to the exact result for hydrogen and to numerically calculated data for helium we estimate the error of the analytic hybrid formula to be less than 5% for moderate energies up to a few hundred eV.

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