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Resonance Contributions to the Photoionization Spectrum of Atomic Hydrogen in an Electric Field

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The photoionization cross section of hydrogen in an electric field is calculated as the sum of resonance contributions, apart from background. Each contribution is proportional to the imaginary part of the square of a complex transition-dipole matrix element divided by an energy denominator and has an asymmetric line shape that is the superposition of dispersive and absorptive Lorentzians. The main features of experiments on the ground and $n=2$ states, including asymmetry of the lines and blue shift of maxima with respect to calculated resonances near zero energy, are reproduced *ab initio*.

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In an electric field the bound states of hydrogen turn into resonances,[1] which can be calculated to high accuracy by complex-coordinate methods[2,3] as well as by "exact numerical solution" of the Schrödinger equation.[4,5] Nevertheless, as pointed out in Ref. 6, "to compare calculated values for resonance energies and widths with experimental data, one needs an analytic line-shape expression, or a procedure for weighting the poles in the complex plane to represent phenomena on the real energy axis." To our knowledge, this problem has remained an open question, which we seek to solve.

Theoretical analyses of photoionization experiments[6-10] have been carried out by perturbation theory,[7] by numerical solution of the Schrödinger equation,[5,11-13] and by Jeffreys-Wentzel-Kramers-Brillouin semiclassical methods,[14-17] among others.[18] The asymmetry of peaks in the spectrum and apparent shifts of maxima from calculated resonance positions, particularly above zero-field ionization potential, have attracted special attention,[5,6] and various parametrizations valid in limited ranges have been given[14-16] that attempt to interpret the spectrum in terms of nearby resonances.

By considering an exactly solvable model,[19] we have recently been able to derive the exact expansion of the photoionization cross section $\sigma(E)$ as a sum of resonance contributions plus background,

$$\sigma(E)=B(E)-\frac{4\pi\omega}{c}\sum_{n=1}^{\infty}\mathrm{Im}\frac{\mu_{0,n}^2}{E-E_n} \tag{1}$$

(E_n in the lower half energy plane). The index n runs over all the resonances E_n in the lower half energy plane. The $\mu_{0,n}$ denotes the complex transition-dipole matrix element between the bound state and the nth resonance, calculated along a path such that the resonance eigenfunction is square integrable. The $\omega=E-E_0$ is the photon energy, with E_0 the energy of the bound state being ionized. The $B(E)$ represents a slowly varying background term. We use units such that $\hbar=m=e=1$.

We show in this paper that the same expansion (1) holds for hydrogen in an electric field, and we apply it to calculate *ab initio* the experimentally observed $\sigma(E)$. Equation (1) is similar in structure to the well-known expansion of the elastic scattering cross section rigorously proved for finite-range potentials by Humblet[20] and by Humblet and Rosenfeld.[21] Both are essentially Mittag-Leffler expansions, which accounts for the similarity. What is notably new and different here, however, is that the coefficients (residues) of the Mittag-Leffler expansion are identified as squared complex transition-dipole matrix elements calculated along appropriate paths in the complex plane, which is both distinctive of the photoionization cross section, and which provides an explicit recipe to compute the spectrum from the resonance wave functions.

A most important consequence of Eq. (1) is that the line shape of isolated resonances is essentially the superposition of a dispersive and an absorptive Lorentzian —what is sometimes called a Fano[22] profile, although no Fano mechanism is present. That is, one can write the resonance contribution as

$$-\mathrm{Im}\frac{\mu_{0,n}^2}{E-E_n} = |\mu_{0,n}^2|\,\frac{\cos\theta(-\mathrm{Im}E_n)-\sin\theta(E-\mathrm{Re}E_n)}{(E-\mathrm{Re}E_n)^2+(\mathrm{Im}E_n)^2}\,, \tag{2}$$

where θ is defined by

$$\theta=2\arg\mu_{0,n}\,. \tag{3}$$

By contrast, if the weighting of the standard Lorentzian profile for the resonance were the square of the modulus of the transition-dipole matrix element, one would have the inappropriate expression

$$\frac{|\mu_{0,n}|^2(-\mathrm{Im}E_n)}{(E-\mathrm{Re}E_n)^2+(\mathrm{Im}E_n)^2}=-\mathrm{Im}\frac{|\mu_{0,n}|^2}{E-E_n} \neq -\mathrm{Im}\frac{\mu_{0,n}^2}{E-E_n}\,. \tag{4}$$

Tacit assumption that the observed photoionization profile should exhibit maxima at the resonance positions has led to questioning the accuracy of experiments.[5] It is clear, however, that when the profile is significantly dispersive, the maximum does not occur at the (real part of the) resonance position. Furthermore, the dispersive component decreases only as $1/(E-\mathrm{Re}E_n)$, not $1/(E-\mathrm{Re}E_n)^2$, and consequently resonances that may seem well separated in fact overlap, changing substantially the composite cross section from that of isolated resonances. This is what happens in hydrogen (cf. Fig. 2) (see also Fig. 7 of Ref. 19 for a simple example).

The rigorous derivation of the expansion of $\sigma(E)$ in the "double-δ-function" model[19] is a straightforward application of complex-variable theory made possible by the meromorphic structure of $\sigma(E)$ as a function of $k=(2E)^{1/2}$. To adapt the derivation in the double-δ model for hydrogen, we start with the expression[7] of $\sigma(E)$ as the square of the transition-dipole matrix element between the initial state and energy-δ-function normalized continuum state,

$$\sigma(E)=\frac{4\pi^2\omega}{c}\langle\psi_0|z|\psi_E\rangle\langle\psi_E|z|\psi_0\rangle\,, \tag{5}$$

and manipulate its using complex-variable theory.[23] To be able to analytically continue the right-hand side of Eq. (5), the continuum wave function ψ_E is chosen to be the product of a real function times $e^{im\phi}$, ϕ being $\arctan(y/x)$, and the scalar products are to be taken without complex conjugation of the left (bra) function, but with the sign of m reversed.

The first step is to apply Cauchy's formula,

$$\sigma(E)=\frac{4\pi^2\omega}{c}\frac{1}{2\pi i}\oint_{|E'-E|=\epsilon}dE'\frac{\langle\psi_0|z|\psi_{E'}\rangle\langle\psi_{E'}|z|\psi_0\rangle}{E'-E}\,. \tag{6}$$

We substitute for the circular integration path the difference of two indented paths from $-\infty$ to $+\infty$ to obtain

$$\sigma(E)=\frac{4\pi^2\omega}{c}\frac{1}{2\pi i}\left[\int_{-\infty}^{+\infty}dE'\frac{\langle\psi_0|z|\psi_{E'}\rangle\langle\psi_{E'}|z|\psi_0\rangle}{E'-E-i\epsilon}-\int_{-\infty}^{+\infty}dE'\frac{\langle\psi_0|z|\psi_{E'}\rangle\langle\psi_{E'}|z|\psi_0\rangle}{E'-E+i\epsilon}\right], \tag{7}$$

$$\sigma(E)=\frac{4\pi^2\omega}{c}\frac{1}{2\pi i}\left[\langle\psi_0|z\frac{1}{H-E-i\epsilon}z|\psi_0\rangle-\langle\psi_0|z\frac{1}{H-E+i\epsilon}z|\psi_0\rangle\right]. \tag{8}$$

At this point in the double-δ model, explicit, specific knowledge of the analytic structure permitted expansion of the resolvent matrix element as a sum over resonances plus background. In the present case, hydrogen in a uniform electric field F, we have from Herbst[24] the implicit, general result that for the Hamiltonian

$$H=-\tfrac{1}{2}\nabla^2-1/r+Fz\,, \tag{9}$$

matrix elements of $(E-H+i\epsilon)^{-1}$, which are analytic in the upper half E plane, admit (via complex rotation of the coordinates) a meromorphic continuation to the entire complex plane, with the only singularities being simple poles in the lower half plane at the resonance eigenvalues. Herbst's result permits a partial fraction expansion of the matrix elements of the resolvent by applying Cauchy's theorem to a contour enclosing E and the first N resonances:

$$\langle\psi_0|z\frac{1}{E-H+i\epsilon}z|\psi_0\rangle=\sum_n^N\frac{\langle\psi_0|z|\psi_n\rangle^2}{E-E_n}+\frac{1}{2\pi i}\oint_{\Gamma_N}\frac{dE'}{E'-E}\langle\psi_0|z\frac{1}{E'-H+i\epsilon}z|\psi_0\rangle\,. \tag{10}$$

The residues, as indicated in Eq. (10), turn out to be the squares of the complex transition matrix elements between the bound state and the complex rotated (square integrable, normalized) resonance wave functions ψ_n. The matrix element of $(E-H-i\epsilon)^{-1}$ gives a similar contribution from the corresponding resonances in the upper half plane, and the two terms in square brackets in Eq. (8) are complex conjugates of each other when E is real. In such a way one obtains Eq. (1), with $B(E)$ given by

$$B(E)=\lim_{N\to\infty}\frac{-4\pi\omega}{c}\,\mathrm{Im}\oint_{\Gamma_N}\frac{dE'}{E'-E}\langle\psi_0|z\frac{1}{E'-H+i\epsilon}z|\psi_0\rangle\,. \tag{11}$$

In contrast with the exactly solvable model,[19] we emphasize that the previous derivation is merely formal: There is an implicit assumption of nondegeneracy, and, since we do not have an explicit formula or even a bound for the right-hand side of Eq. (11), we have been unable to prove that the limit exists.[25]

We report *ab initio* calculations based on Eq. (1) to interpret two very different photoionization experiments with polarization parallel to the static field: (i) for the ground state in a static field $F=2.61$ MV/cm, photoionized to an energy just above the classical saddle-point energy, $-2F^{1/2}$ in atomic units (Ref. 6), and (ii) for the state with parabolic quantum numbers $(n_1,n_2,m)=(1,0,0)$ in a field of 5714 V/cm, photoionized to an energy in a neighborhood of the zero-field ionization potential (Ref. 7). The first case is an example of the cross section dominated by a single resonance, with quantum numbers $(n_1,n_2,m)=(0,3,0)$, while in the second case many overlapping resonances must be considered.

The idea of the calculational procedure is as follows: The coordinates in the Hamiltonian [Eq. (9)] are rotated into the complex plane, giving rise to a non-self-adjoint eigenvalue problem. The (now square integrable) resonance eigenfunctions are expanded in an appropriate discrete basis, and the expansion coefficients are determined by matrix diagonalization methods. In practice we carry out the calculation in parabolic coordinates to take advantage of the separability. The details are given in Ref. 25.

The wave function and energy for the (0,3,0) resonance and the transition dipole connecting it to the ground state were calculated as sketched above. The results,

$$E_{(0,3,0)} = -0.042\,112\,718 - i0.000\,270\,258 \text{ a.u.}$$

$$= -1.146\,5789 - i0.014\,7163 \text{ eV}, \qquad (12)$$

$$\mu_{0;(0,3,0)} = -0.087\,250\,663 + i0.010\,898\,130 \text{ a.u.}, \qquad (13)$$

were then substituted into Eq. (2) and plotted in Fig. 1 (curve *a*). (The vertical scale is arbitrary.) Figure 1 (curve *b*) is obtained by convolution of the theoretical Fig. 1 (curve *a*) with the instrumental line-shape function (the details of which were taken from Ref. 16). The experimental data are also plotted with error bars for the standard deviations.[26] It is clear that the theoretically calculated single resonance contribution accounts for the major features of the experimental spectrum: the asymmetric profile with higher "base line" on the high-energy side.

For the Rottke-Welge experiment[7] we consider the region between -125 and $+50$ cm^{-1}. We have calculated variationally the complex wave functions and energies of the fourteen sharpest resonances in this region (and a fifteenth at 59 cm^{-1}), along with the (1,0,0) initial state, and the corresponding transition-dipole matrix elements. The results are plotted in Fig. 2. In this case the theory has not been convoluted with an instrumental line-shape function, but the tops of the sharpest lines have been cut off to show the detailed structure at a reasonable scale. The triangles mark the positions of the calculated real parts of the resonances. Notice that for the sharp lines, which are relatively symmetric, the triangles fall close to the maxima. For the broader lines, especially above the zero-field ionization energy, *the line shape of single resonances is significantly dispersive, and the triangles fall between the maxima and minima of the composite cross section.* With one exception, we have not included contributions from other broader resonances, whose primary importance here would be in building up the base line. The exception is the contribution of the (26,0,0) resonance near 59 cm^{-1} that alters the base line and line shape in the region near the (25,0,0) resonance at ~34 cm^{-1}. As mentioned above, the overlap of the wings of dispersive resonances substantially changes the appearance of the local line shape (again, cf. Fig. 7 of Ref. 19).

Comparison of the theoretical Fig. 2 with the experimental Fig. 4(a) of Ref. 7 shows excellent agreement with the positions, widths, and line shapes of the peaks, from the very narrow near -125 cm^{-1} to the broad structure above the zero-field ionization threshold. What is especially important is that the "field-induced modulations" are resonance contributions calculated on an equal footing with the sharp "LoSurdo-Stark" peaks.

In summary, the contribution of each resonance to the photoionization cross section, as given by Eq. (2) and as calculated variationally from first principles, is an asymmetric combination of dispersive and absorptive Lo-

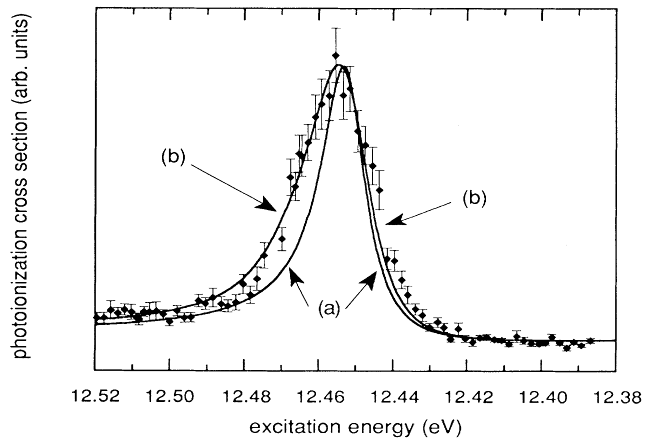

FIG. 1. Contribution of the (0,3,0) resonance to the photoionization cross section of the ground state of hydrogen in a field of 2.61 MV/cm: (curve *a*) the theoretical contribution of (0,3,0), calculated via Eq. (2) from the *ab initio* resonance eigenfunction; (curve *b*) theoretical contribution convoluted with the instrumental line-shape function; ◆ with error bars indicate the experimental points.

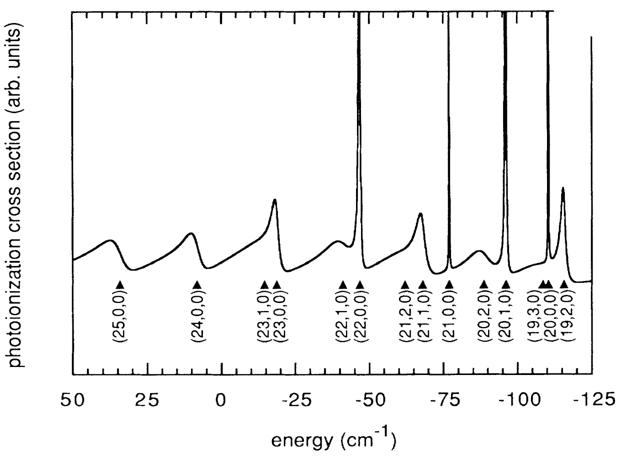

FIG. 2. Contributions from fourteen resonances in the range -125 to $+50$ cm^{-1} to the photoionization cross section of the (1,0,0) state of hydrogen in a static field of 5714 V/cm. The triangles mark the positions of the real parts of the resonances. There is a fifteenth resonance at 59 cm^{-1} that is also included in the calculation.

rentzians, whose relative weights are determined by the argument of the complex transition moment. The sum of such contributions [Eq. (1)] accounts for the most prominent features for hydrogen in an electric field, both below and above the zero-field ionization potential.

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