Photoelectron motion in the presence of a probe electromagnetic wave

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Photoionization in the presence of a probe electromagnetic wave is studied. A continuum wave function is obtained in a weak-field, low-frequency limit for low-energy photoelectrons. When the electron and photon energies are comparable, the absorption and stimulated-emission angular distributions show a significant departure from results based on a much-used on-shell approximation of Kroll and Watson.

I. INTRODUCTION

There has been recent work[1] on the effect of a strong radiation field on autoionizing levels embedded in the photoelectron continuum. The emphasis of this work is on the laser coupling of the autoionizing level with the continuum and the resulting modification of the Fano line profile,[2] which, in the absence of the radiation field, is characteristic of photoabsorption near one of these levels. It is the purpose of this paper to examine the effect of a strong field on the photoelectron continuum wave function in the absence of an autoionizing level.

The strong field is produced by a second, low-frequency laser which probes a target which is being ionized by a weak source. At the power levels used here, the second laser has a negligible effect on the initial orbital (demonstrated below). There has already been some work[3] on laser modulation of photoionization; however, this work is for energetic ionizing photons which produce fast photoelectrons. The latter are described by a wave function which is calculated in the well-known on-shell approximation studied by Kroll and Watson[4] for electron scattering (or, more appropriately, in an on-shell approximation as modified for a Coulomb field by Fiordilino and Mittleman[5]).

The present work is motivated by the thought that "resonant" continuum wave functions (whether of the many-body[2] or shape[6,7] type) can have their resonant behavior confined to a single partial wave which is strongly varying with energy through the resonance. The radiation field, on the other hand, destroys l as a good quantum number. For example, a CO_2 laser with intensity of about 6 MW cm^{-2} produces an oscillating dipolar field whose dipole moment is about 1.7 D. Thus a theory should be formulated in which the photoelectron partial waves are coupled by the field (in analogy to the theory of photoionization of a polar molecule). The oscillation of the dipolar field means that the principal effect is absorption and stimulated emission by the photoelectron.[3] Furthermore, for low-energy photoelectrons, such that the low-frequency probe photon and photoelectron energies are comparable, the cross section is found to deviate significantly from the on-shell result of Kroll and Watson.[3,4]

II. THEORY

Photoionization by the weak source is treated perturbatively, such that the probability amplitude for the final state is

$$a_{\vec{k}}(t)=\frac{1}{i}\int_0^t dt'\langle\psi_{\vec{k}}(\vec{r},t')\,|\,\tfrac{1}{2}\Omega_1\,|\,\psi_i(\vec{r},t')\rangle \times e^{-i(\omega_0+\omega_1)t'}, \tag{1a}$$

$$\Omega_1=\left[\frac{8\pi F_1\alpha}{\omega_1}\right]^{1/2}\frac{\hbar}{m}\hat{\rho}_i(i\vec{\nabla}), \tag{1b}$$

where for the jth source F_j is the flux, ω_j the frequency, $\hat{\rho}_j$ the unit vector in the direction of polarization, and where ω_0 is the frequency of the initial level. The intense source has the interaction Hamiltonian,

$$V_2=\hbar\Omega_2\cos(\omega_2 t), \tag{2}$$

where we have dropped the quadratic term $e^2A^2/(2mc^2)$ since it does not affect the results. Note also that we assume that both sources have sufficiently low frequencies that the photon momentum $\hat{k}_j\hbar\omega_j/c$ is negligible.

First we show that (for the second laser power levels envisioned here) the distortion of the initial state can be ignored (provided ω_2 is small compared to target internal frequencies), such that ψ_i can be replaced by the unperturbed, time-independent wave function ψ_{i0}. The first-order correction to ψ_{i0} is

$$\psi_{i1}=\sum_j\psi_{j0}(\vec{r})\int\frac{d\vec{r}\,'\psi^*_{j0}(\vec{r}\,')(\frac{1}{2}\Omega_2)\psi_{i0}(\vec{r}\,')}{\omega_0-\omega_j+\omega_2} \times e^{-i(\omega_0+\omega_2)t}, \tag{3}$$

where the sum runs over the complete set of unperturbed states and we consider only the absorptive term in the interaction. We estimate the size of the first-order correction (for a hydrogenic atom) by assuming that $\omega_2-\omega_j$ is small compared to ω_0. Using closure, we find that $(2\pi F_2\alpha/\omega_2)^{1/2}(2a_0/Z)$ or $1.114\times10^{-17}(F_2/E_2)^{1/2}$ (where E_2 is the second-laser photon energy in a.u.) must

be small compared to one for ψ_{i1} to be small compared to ψ_{i0}. For the CO_2 laser (0.117-eV photons), this number is $1.7\times10^{-16}F_2^{1/2}$.

On the other hand, the first-order correction to the continuum wave function is

$$\psi_{\vec{k}1}=(2\pi)^{-3}\int d\vec{k}'\int d\vec{r}'\frac{\psi_{\vec{k}'0}(\vec{r})\psi^*_{\vec{k}'0}(\vec{r}')(\frac{1}{2}\Omega_2)\psi_{\vec{k}0}(\vec{r}')}{\frac{\hbar k^2}{2m}-\frac{\hbar k'^2}{2m}+\omega_2}\times\exp\left[-i\left[\frac{\hbar k^2}{2m}+\omega_2\right]t\right], \tag{4}$$

where the $\vec{k}'$ integration is over the unperturbed continuous set. Using plane waves for the continuum wave functions, the integrations over $\vec{r}'$ and $\vec{k}'$ are carried out giving the result that $(2\pi F_2\alpha/\omega_2)^{1/2}(\hbar k/m\omega_2)$ or (using $k=0.1a_0^{-1}$ for low-energy photoelectron) $5.571\times10^{-19}F_2^{1/2}/E_2^{3/2}$ must be small compared to one for $\psi_{\vec{k}1}$ to be small compared to $\psi_{\vec{k}0}$. For CO_2 photons this number is $2.0\times10^{-15}F_2^{1/2}$. In this calculation, the maximum F_2 is about 0.36×10^{28} cm^{-2}s^{-1}, such that the ratio of the continuum to bound validity criteria is 0.12 to 0.01, respectively. The correction to the continuum is more than an order of magnitude greater under these circumstances since the denominator in Eq. (4) reduces to ω_2 when the integrations over $\vec{r}'$ and $\vec{k}'$ are performed.

In Eq. (1a) the continuum wave function has the integral equation,[4]

$$\psi_{\vec{k}}(\vec{r},t)=\chi_0(\vec{r},t)+\int d\vec{r}'\int_{-\infty}^{t}dt'G_0(\vec{r},\vec{r}',t,t')V(\vec{r}')\psi_{\vec{k}}(\vec{r}',t'), \tag{5a}$$

$$G_0=(i\hbar)^{-1}(2\pi)^{-3}\int d\vec{k}'\exp^{[i\vec{k}'\cdot(\vec{r}-\vec{r}')]}\exp\left[-\frac{i\hbar k'^2}{2m}(t-t')\right]\exp^{\{i\vec{k}'\cdot\vec{R}[\sin(\omega_2t)-\sin(\omega_2t')]\}}, \tag{5b}$$

$$\chi_0=\exp^{(i\vec{k}\cdot\vec{r})}\exp\left[-\frac{i\hbar k^2}{2m}t\right]\exp^{[i\vec{k}\cdot\vec{R}\sin(\omega_2t)]}. \tag{5c}$$

$\psi_{\vec{k}}$ exactly solves the Schrödinger equation,

$$\left[i\hbar\frac{\partial}{\partial t}-H_0\right]\psi_{\vec{k}}(\vec{r},t)=V(\vec{r})\psi_{\vec{k}}(\vec{r},t), \tag{6a}$$

$$H_0=-\frac{\hbar^2}{2m}\nabla^2+V_2, \tag{6b}$$

where V is a local,[8] electron-target potential of shorter range than r^{-1} (restricting the theory to the photodetachment of negative ions). The second term in Eq. (6b) may be more transparent if it is reexpressed,

$$V_2=i\hbar\omega_2\cos(\omega_2t)\vec{R}\cdot\vec{\nabla}, \tag{7a}$$

$$\vec{R}=\left[\frac{8\pi F_2\alpha}{\omega_2}\right]^{1/2}\frac{\hbar}{m\omega_2}\hat{\rho}_2, \tag{7b}$$

in terms of a dipole moment $e\vec{R}$ due to the second radiation field. This form emphasizes that dipolar coupling of the photoelectron partial waves should be considered in a low-energy theory of photoionization. That $\psi_{\vec{k}}$ solves Eq. (6a) is readily verified by substituting Eq. (5a) into the left-hand side of Eq. (6a).

The formal properties of Eq. (5a) have been studied by Kroll and Watson[4] for electron scattering. For large r the exact scattering amplitude is given. These authors then use stationary phase arguments to derive the widely used[9] on-shell approximation for the amplitude. Photoeffect studies to date[3,5] use an appropriate on-shell approximation for the photoionization amplitude. These approximations are not valid for comparable electron-photon energies, which is the situation for the production of low-energy photoelectrons by the first source. Much progress has been made recently[10] in the numerical solution of coupled integral equations in field-free low-energy photoionization studies; thus it would appear worthwhile to attempt the numerical solution of Eq. (5a).

The expansions

$$\psi_{\vec{k}}(\vec{r},t)=\sum_{p=-\infty}^{\infty}\psi_{\vec{k}p}(\vec{r})e^{-i(\hbar k^2/2m-p\omega_2)t}, \tag{8a}$$

$$e^{\pm i\vec{k}\cdot\vec{R}\sin(\omega_2t)}=\sum_{q=-\infty}^{\infty}J_q(\vec{k}\cdot\vec{R})e^{\pm iq\omega_2t}, \tag{8b}$$

are substituted into Eqs. (5). From Eq. (8a) it is clear that $|p|$ photons are absorbed ($p<0$) or emitted ($p>0$) [where it is assumed that $(\hbar k^2/2m-p\omega_2)>0$]. It is straightforward to derive the set of coupled time-independent equations,

$$\psi^{(-)}_{\vec{k}p}=e^{i\vec{k}\cdot\vec{r}}J_p(\vec{k}\cdot\vec{R})+\lim_{\epsilon\to0}(2\pi)^{-3}\sum_{n=-\infty}^{\infty}\sum_{q'=-\infty}^{\infty}\int d\vec{k}'\int d\vec{r}'e^{i\vec{k}'\cdot(\vec{r}-\vec{r}')}\frac{J_{p-n}(\vec{k}'\cdot\vec{R})J_{q'}(\vec{k}'\cdot\vec{R})V(\vec{r}')\psi^{(-)}_{\vec{k}n+q'}(\vec{r}')}{\left[\frac{\hbar^2}{2m}(k^2-k'^2)-n\hbar\omega_2\right]-i\epsilon}, \tag{9}$$

where we have specialized to incoming boundary conditions for use of Eqs. (8a) and (9) in Eq. (1a). When $R=0$, only

$\psi^{(-)}_{\vec{k}0}$ exists, and Eq. (9) reduces to the familiar integral equation of field-free photoionization.[10]

It would be an arduous task to obtain the general solution to Eq. (9). For the present, power levels and electron energies are chosen such that small argument expansions can be used for the Bessel functions and terms retained through order kR. The elastic ($p=0$) wave function is affected at order $(kR)^2$ and higher, so that the field-free $\psi^{(-)}_{\vec{k}0}$ is calculated. On the other hand, for $p=\pm1$ the following coupled, integral radial equation (all of whose terms are of order kR) are obtained for the inelastic wave function (assuming that V is spherically symmetric and that $\vec{R}$, in the direction of $\hat{\rho}_2$, is along the laboratory-frame z axis):

$$\psi^{(-)}_{\pm1ll_j0}(r,k)=\pm i^l j_l(kr)(\tfrac{1}{2}kR)(2l+1)^{1/2}(2l_j+1)^{1/2}\begin{bmatrix} l & 1 & l_j \\ 0 & 0 & 0 \end{bmatrix}^2$$

$$+\int_0^\infty dr'r'^2 g^{(-)}_{\pm1ll}(r,r')U(r')\psi^{(-)}_{\pm1ll_j0}(r',k)$$

$$\pm i^{l-l_j}(2l+1)^{1/2}(2l_j+1)^{1/2}\begin{bmatrix} l & 1 & l_j \\ 0 & 0 & 0 \end{bmatrix}^2\int_0^\infty dr'r'^2[(\tfrac{1}{2}kR)g^{(-)}_{0ll_j}(r,r')$$

$$-(\tfrac{1}{2}k_{\pm1}R)g^{(-)}_{\pm1ll_j}(r,r')]U(r')\psi^{(-)}_{0l_jl_j0}(r',k)\ , \tag{10a}$$

$$g_{pll_j}(r,r')=k_p[n_l(k_pr)j_{l_j}(k_pr')+j_l(k_pr)n_{l_j}(k_pr')+ij_l(k_pr)j_{l_j}(k_pr')]\ , \tag{10b}$$

$$\frac{k_p^2}{2}=\frac{k^2}{2}-pE_2\ , \tag{10c}$$

where $r>r'$ and $r<r'$ in the first and second terms of Eq. (10b), respectively, and where the expansion

$$\psi_{\vec{k}p}=4\pi\sum_{ll_jm}\psi^{(-)}_{pll_jm}(r,k)Y_{lm}(\theta_r,\phi_r)Y^*_{l_jm}(\theta_k,\phi_k) \tag{11}$$

has been used. In Eq. (1a) it is assumed that $\psi_i=\psi_{i0}$ is an S state, such that, for $\hat{\rho}_1$ parallel to the laboratory-frame z axis (and therefore to $\hat{\rho}_2$), only the $m=0$ components of Eq. (11) contribute to the matrix element. Using Eqs. (1), (8a), and (11), it is straightforward to obtain the angular distributions of photoelectrons for the $p=\pm1$ processes,

$$\frac{d\sigma_{\pm1}}{d\Omega}=\frac{2\alpha a_0^2k}{3E_1}[\,|R^{(\pm1)}_{10}|^2+5|R^{(\pm1)}_{12}|^2P_2^2(\cos\theta_k)$$

$$+2\sqrt{5}\,\mathrm{Re}R^{(\pm1)*}_{10}R^{(\pm1)}_{12}P_2(\cos\theta_k)]\ , \tag{12a}$$

$$R^{(\pm1)}_{1l_j}=\int_0^\infty dr\,r^2\psi^{(-)*}_{\pm1ll_j}(r,k)\left[\frac{d}{dr}\right]\psi_{i0}(r)\ , \tag{12b}$$

$$\frac{k^2}{2}\mp E_2=E_0+E_1\ . \tag{12c}$$

From Eq. (12c) electrons are ejected with energy $k^2_{\pm1}/2=k^2/2\mp E_2$ [see Eq. (10c)]. In Eqs. (10), when $k_{\pm1}\to k$, $R^{(\pm1)}_{10}=\pm(kR/2\sqrt{3})d_1$, and $R^{(\pm1)}_{12}=\pm(kR/\sqrt{15})d_1$, where d_1 is the radial amplitudes for a field-free p wave,

$$d_1=\int_0^\infty dr\,r^2\psi^{(-)*}_{01l0}(r,k)\left[\frac{d}{dr}\right]\psi_{i0}(r)\ . \tag{13}$$

Then Eq. (12a) reduces to the on-shell result,[3,5]

$$\frac{d\sigma_{\pm1}}{d\Omega}=2\alpha a_0^2k/E_1(\tfrac{1}{2}kR)^2|d_1|^2\cos^4\theta_k\ . \tag{14}$$

It remains to show that the expansions in powers of kR are convergent ones. As an example, consider the second term on the right-hand side (rhs) of Eq. (9) for $p=1$, $n=0$, $q'=0$, in which $J_p(\vec{k}'\cdot\vec{R})\simeq(\frac{1}{2}k'R\cos\theta_{k'})^p$. Taking the limit and carrying out the $\vec{k}'$ integration, the rhs contributes terms of the form

$$v_p^{(-)}=\frac{i^p}{4\pi}k(\tfrac{1}{2}kR)^p\int d\vec{r}'[n_p(k|\vec{r}-\vec{r}'|)+ij_p(k|\vec{r}-\vec{r}'|)]P_p(\cos\theta_{r-r'})U(r')\psi^{(-)}_{\vec{k}0}(\vec{r}')\ . \tag{15}$$

We estimate the size of this term by replacing $U(r')$ by a constant U_0 for $0\le r'\le a$ and by zero for $r'>a$ and by evaluating $v_p^{(-)}$ at $r=0$, for small ka, and for an assumed plane wave for $\psi_0^{(-)}$. To order ka, Eq. (15) is of order

$$\frac{(\frac{1}{2}kR)^pU_0a^2}{2[1\times3\times\cdots\times(2p+1)]}\ ,$$

suggesting that, for small kR and ka, the expansion of the integrand in Eq. (9) in powers of $k'R$ and the evaluation of the $\vec{k}'$ and $\vec{r}'$ integrals produce a convergent series in kR (or $k_{\pm1}R$ provided this term is also small).

III. NUMERICAL RESULTS AND DISCUSSION

Equation (10a) is solved iteratively for $U(r')$ equal to a constant U_0 for $0\le r'\le a$ and equal to zero for $r'>a$.

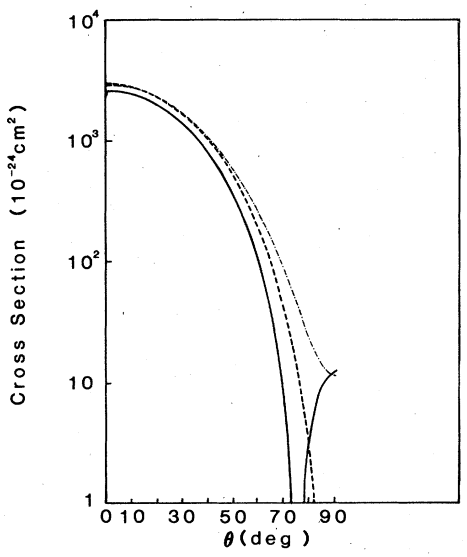

FIG. 1. Solid line, $p=1$ result; dashed line, on-shell approximation; dashed-dotted line, $p=-1$ result.

For $ka=0.7$ and $V_0=-3.530$ a.u., a shape resonance occurs[11] in the p wave. Figure 1 shows results for the photoelectron angular distributions [Eqs. (12a) and (14), where ψ_{i0} is the $1S$ level in this potential with energy $E_0=-2.8645$ a.u.]. The parameter R (where $eR=1.86$ D) is chosen such that $k_{-1}R=0.2$ (for a given flux $F_2=3.43\times10^{26}$ cm^{-2}s^{-1} of the CO_2 laser), and $k_{+1}=0.24a_0^{-1}$ is chosen as the electron momentum (in a.u.) where the field-free, resonant photoelectron cross section approaches its maximum value (1.48 Mb). For CO_2 photons (0.117 eV), Eq. (10c) requires a maximum of ten iterations to coverage.

Note that Eq. (12a) gives results which deviate significantly from the on-shell result of Eq. (14). These deviations are the result of the dipolar coupling of the p wave to s and d waves in the last two terms of Eq. (10a). The uncoupled p wave is resonant; thus the resonance can spread to the other partial waves through this coupling, in analogy to a molecular field effect which has received study.[12] By $k=0.5a_0^{-1}$, however, Eqs. (12a) and (14) nearly agree. These results suggest that the angular distribution maybe the best measurement of the effect of the probe radiation field on photoionization dynamics. The $p=\pm1$ cross sections are small, however, as a result of our small-kR criterion for the solution of Eq. (9). It would appear worthwhile to obtain a more general solution to this equation.

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