Theory of Resonant Multiphoton Ionization*

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The quantum-mechanical method developed earlier is applied to the four-photon resonant ionization of Cs. Comparisons of the present calculations with the experiments by Held *et al.* are given, and good agreement with the experiments is obtained. The application of the present theoretical method to the six-photon ionization of hydrogen is indicated.

Recently Held *et al.*[1] published experimental results on the four-photon ionization of Cs by light of frequency near that required to produce three-photon excitation of the $6f$ state. They found very rapid variation of the transition probability with frequency and with incident intensity. This Letter describes briefly a theoretical calculation which reproduces the experimental results on the two sides of the resonance and at exact resonance. The calculation very near resonance is numerically complicated and is being carried out. The main features are, however, already clear.

The method developed earlier[2,3] is used straightforwardly. The electron propagator in the presence of the incident radiation field, including forward scattering processes, can be written in the notation of I and II as

$$\tilde{G}(x_1, x_2) = \sum_n \tilde{\Psi}_n(\vec{r}_1)\bar{\tilde{\Psi}}_n(\vec{r}_2)\int_{-\infty}^{\infty} \frac{d\Omega}{2\pi i} \frac{\exp[i\Omega(t_1 - t_2)]}{\tilde{E}_n + \Omega + \tilde{H}_{n,n}(-\Omega)}. \tag{1}$$

The tilde denotes the renormalized quantity; $\tilde{H}_{n,n}(-\Omega)$ is the resonant part of $H_{n,n}(-\Omega)$, the nonresonant part being incorporated in the shifted energy $\tilde{E}_n$. Use of this propagator leads to the four-photon ionization amplitude in the form

$$C_{\tilde{6s}\to\tilde{E}}(t) = (e^2N\omega/2V)^2 \sum_{n_1n_2n_3} \langle\tilde{E}|\hat{r}|\tilde{n}_1\rangle\langle\tilde{n}_1|\hat{r}|\tilde{n}_2\rangle\langle\tilde{n}_2|\hat{r}|\tilde{n}_3\rangle\langle\tilde{n}_3|\hat{r}|\tilde{6s}\rangle$$
$$\times \int_{-\infty}^{\infty} (d\Omega/2\pi i) e^{i\Omega t}\{(\tilde{E} + \Omega + i0)(4\omega + \tilde{E}_{6s} + \omega + i0)[\tilde{E}_{n_1} + \omega + \Omega + \tilde{H}_{n_1,n_1}(-\Omega - \omega)]$$
$$\times [\tilde{E}_{n_2} + 2\omega + \Omega + \tilde{H}_{n_2,n_2}(-\Omega - 2\omega)][\tilde{E}_{n_3} + 3\omega + \Omega + \tilde{H}_{n_3,n_3}(-\Omega - 3\omega)]\}^{-1}. \tag{2}$$

The factor $\tilde{E}_{n_1} + \omega + \Omega + \tilde{H}_{n_1,n_1}(-\Omega - \omega)$ is the energy denominator coming from the state after absorption of three photons, and when $|\tilde{n}_1\rangle = |\tilde{6f}\rangle$ is particularly important. This term is therefore separated out:

$$C_{\tilde{6s}\to\tilde{E}}(t) = \tilde{A}(\tilde{E}, t) + \tilde{B}(\tilde{E}, t). \tag{3}$$

$\tilde{B}$ contains all contributions other than the resonant one:

$$\tilde{A}(\tilde{E}, t) = (A/2\pi i)\int_{-\infty}^{\infty} d\Omega\, e^{i\Omega t}\{(\tilde{E} + \Omega)(\tilde{E}_{6s} + 4\omega + \Omega)[\tilde{E}_{6f} + \omega + \Omega + \tilde{H}_{6f,6f}(-\Omega - \omega)]\}^{-1}, \tag{4}$$

$$\tilde{B}(\tilde{E}, t) = (B/2\pi i)\int_{-\infty}^{\infty} d\Omega\, e^{i\Omega t}[(\tilde{E} + \Omega)(\tilde{E}_{6s} + 4\omega + \Omega)]^{-1}, \tag{5}$$

$$A = (e^2N\omega/2V)^2 \sum_{n_2,n_3} \langle\tilde{E}|\hat{r}|\tilde{6f}\rangle\langle\tilde{6f}|\hat{r}|\tilde{n}_2\rangle\langle\tilde{n}_2|\hat{r}|\tilde{n}_3\rangle\langle\tilde{n}_3|\hat{r}|\tilde{6s}\rangle[(\tilde{E}_{n_2} - 2\omega - \tilde{E}_{6s})(\tilde{E}_{n_3} - \omega - \tilde{E}_{6s})]^{-1}, \tag{6}$$

$$B = (e^2N\omega/2V)^2 \sum_{n_2,n_3,n_1\neq 6f} \langle\tilde{E}|\hat{r}|\tilde{n}_1\rangle\langle\tilde{n}_1|\hat{r}|\tilde{n}_2\rangle\langle\tilde{n}_2|\hat{r}|\tilde{n}_3\rangle\langle\tilde{n}_3|\hat{r}|\tilde{6s}\rangle$$
$$\times [(\tilde{E}_{n_1} - 3\omega - \tilde{E}_{6s})(\tilde{E}_{n_2} - 2\omega - \tilde{E}_{6s})(\tilde{E}_{n_3} - \omega - \tilde{E}_{6s})]^{-1}. \tag{7}$$

The quantity $\tilde{H}_{6f,6f}$ is obtained principally from the forward scattering process in which three photons are emitted leading to $6s$ and then three photons are absorbed:

$$\tilde{H}_{6f,6f}(-\Omega) = -\xi^2/(\tilde{E}_{6s} + 3\omega + \Omega), \quad \xi^2 \propto I^3. \tag{8}$$

The shifted energy $\tilde{E}_{6f}$ can be written

$$\tilde{E}_{6f} = \tilde{E}_{6f}' + i\gamma_{6f}, \tag{9}$$

where γ_{6f} is positive and comes from the imaginary part of the single forward scattering process $|6f\rangle + \omega \rightarrow |E\rangle \rightarrow |6f\rangle + \omega$. It is proportional to $I = N\omega/V$, the laser intensity.

In units with $\hbar = c = 1$, and measuring I in cm^{-4} ($1\ \mathrm{W/cm^2} = 1.058\times10^{13}\ \mathrm{cm}^{-4}$), the desired quantities are[4]

$$\gamma_{6f} = e^2\pi I[\rho(E)|\langle E|\hat{r}|6f\rangle|^2]_{E=E_{6f}+\omega} \approx 0.35\times10^{-22} I\ \mathrm{cm}^{-1}, \tag{10}$$

$$\xi^2 = I^3\left|\sum_{n_2,n_3}\frac{\langle 6f|e\hat{r}|n_2\rangle\langle n_2|e\hat{r}|n_3\rangle\langle n_3|e\hat{r}|6s\rangle}{(E_{6f}-\omega-E_{n_2})(E_{6f}-2\omega-E_{n_3})}\right|^2 \approx 10^{-69} I^3\ \mathrm{cm}^{-2}, \tag{11}$$

$$\tilde{E}_{6s} - E_{6s} = H_{6s,6s}{}' = -(2.77\times10^{-22} I + 1.33\times10^{-46} I^2 + 8.2\times10^{-72} I^3)\ \mathrm{cm}^{-1}, \tag{12}$$

$$\tilde{E}_{6f}{}' - E_{6f} = H_{6f,6f}{}' = (0.72\times10^{-22} I + 1.62\times10^{-47} I^2 + 1.3\times10^{-72} I^3)\ \mathrm{cm}^{-1}, \tag{13}$$

$$\beta = B/A \approx 0.021\ \mathrm{cm}. \tag{14}$$

The quantities $\tilde{A}$ and $\tilde{B}$ are

$$\tilde{A}(\tilde{E}, t) = \frac{Ae^{-i\tilde{E}t}}{(z - \frac{1}{2}i\gamma_{6f})^2 - \frac{1}{4}\eta^2}\left\{1 - \exp(-izt - \tfrac{1}{2}\gamma_{6f}t)\left[\cos\frac{\eta t}{2} + \left(\frac{2iz+\gamma_{6f}}{\eta}\right)\sin\frac{\eta t}{2}\right]\right\}, \tag{15}$$

$$\tilde{B}(\tilde{E}, t) = [Be^{-i\tilde{E}t}/(\tilde{E} - \tilde{E}_{6s} + 4\omega)]\{\exp[-i(\tilde{E}_{6s} + 4\omega - \tilde{E})t] - 1\}, \tag{16}$$

where

$$z = \tfrac{1}{2}[(\tilde{E} - \tilde{E}_{6f}{}' - \omega) + (\tilde{E} - \tilde{E}_{6s} - 4\omega)], \tag{17}$$

$$\eta^2 = (\eta_1 + i\eta_2)^2 = (\Delta - i\gamma_{6f})^2 + 4\xi^2, \tag{18}$$

$$\Delta = \tilde{E}_{6f}{}' - \tilde{E}_{6s} - 3\omega, \tag{19}$$

$$\eta_1{}^2 = \tfrac{1}{2}\{[\Delta^2 + (\gamma_{6f} - 2\xi)^2]^{1/2}[\Delta^2 + (\gamma_{6f} + 2\xi)^2]^{1/2} + \Delta^2 - \gamma_{6f}{}^2 + 4\xi^2\}, \tag{20}$$

$$\eta_2{}^2 = \eta_1{}^2 - \Delta^2 + \gamma_{6f}{}^2 - 4\xi^2. \tag{21}$$

The transition probability is found by squaring the amplitude, summing over final states, and averaging over the interaction time, which is the time spent by the atom in the focal volume. The velocity is distributed according to v times a Maxwellian speed distribution. Finally the result is averaged over the laser frequency width γ_l. Thus

$$P(t) = \int d\tilde{E}\,\rho(\tilde{E})|C_{\tilde{6}s\rightarrow\tilde{E}}(t)|^2, \tag{22}$$

$$\langle P(\omega)\rangle = \tfrac{1}{2}M^2(kT)^2\int_0^\infty dv\, v^3 P(l/v)\exp(-Mv^2/2kT), \tag{23}$$

$$\bar{P}(\Delta, I) = (\gamma_l/2\pi)\int_{-\infty}^{\infty} dx\,\langle P(\omega + x)\rangle/(x^2 + \tfrac{1}{4}\gamma_l{}^2). \tag{24}$$

Off resonance the exponentially damped term in (11) can be neglected. Then

$$\bar{P}(\Delta, I) \approx [4\pi A^2\rho(0)/\gamma_{6f}]\{[\Delta^{-1} + \tfrac{1}{2}\zeta(2+\sqrt{2})]^2 + \tfrac{1}{4}\zeta^2[\gamma_{6f}\tau - 2(3+2\sqrt{2})]\}, \tag{25}$$

with $\tau = (\pi M l^2/8kT)^{1/2}$. At resonance, $\Delta = 0$, (16) can be neglected, and (24) may be approximated by

$$\bar{P}(0, I) \approx \pi A^2\rho(0)\tau/4\gamma_{6f}{}^2. \tag{26}$$

In a log-log plot of $\bar{P}(\Delta, I)$ for fixed Δ, the slope is given by

$$K = \partial\log\bar{P}(\Delta, I)/\partial\log I. \tag{27}$$

Let the effective interaction length $l \approx 0.5\times10^{-3}$ cm, $T \approx 1200$°K, and $I = 1.4\times10^{8}\ \mathrm{W\,cm^{-2}}$, then $\tau \approx 10^{-8}$ sec. We find (25) has a minimum at $\Delta \approx -28\ \mathrm{cm}^{-1}$. Remembering $A \propto I^2$ and $\gamma_{6f} \propto I$, we find the values of $K \approx 8$, 5.5, and 3.2 at $\Delta \approx -28$, -60, and $30\ \mathrm{cm}^{-1}$, respectively. The ratio of the minimum to the maximum calculated from (25) and (26) is found to be about 4×10^{-6}. All these quantitative results are in satisfactory agreement with experiments.[1] The functions $\bar{P}(\Delta, I)$ and K are plotted in Figs. 1 and 2.

There are some features of the calculation just sketched of special interest. The intensity dependence is not a simple fourth-power law as it would be far from resonance because the intensity enters

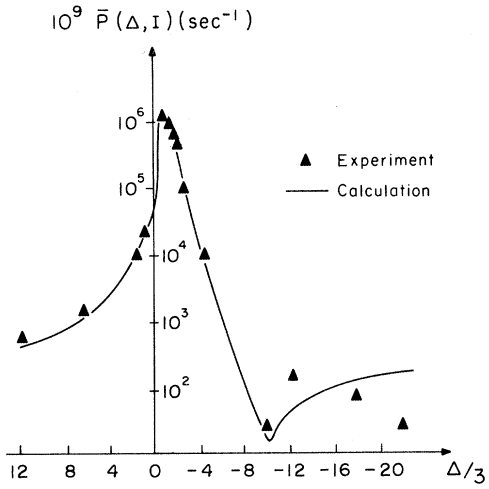

FIG. 1. Variation of four-photon ionization probability $\bar{P}(\Delta, I)$ as a function of the laser frequency detuning for a given laser intensity $I = 1.4\times10^8$ W cm^{-2}, assuming the number of Cs atoms crossing the focal area to be 10^9 sec^{-1}. The experimental points are taken from Ref. 1. The relative level shift between $6s$ of $6f$ levels is found to be about 0.3 cm^{-1}.

the level shifts and widths. The minimum in the transition probability comes from the interference between the resonant and nonresonant amplitudes. It is near this minimum that the intensity dependence is greatest. The form of the expression (15) for the resonant amplitude results from the presence of three poles in the Ω integration of this term. The form of (15) is much like that of the Rabi formula for a two-level system but is complicated by the presence of the width γ_{6f} absent in the Rabi formula[5] where no transition to the continuum is included. In the case of six-photon ionization of hydrogen,[6] the laser frequency is far from resonance with the bare hydrogen levels, but the intensity-dependent shifts cause the physical states to be near resonance with the laser frequency at a sufficiently high intensity. The method here indicated can therefore be directly applied. The details will given elsewhere.

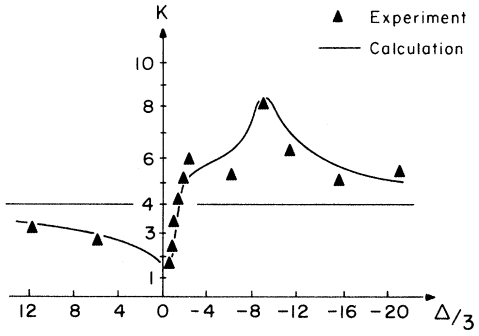

FIG. 2. Variation of the slope K as a function of the laser frequency detuning. Minimum occurs at laser frequency 9444 cm^{-1}, $K \approx 2$. Maximum occurs at laser frequency 9452 cm^{-1}, $K \approx 8$. $I = 1.4\times10^8$ W cm^{-2} as in Fig. 1. The experimental points are taken from Ref. 1.

Because of the angular momentum of the resonant state, the resonant contribution to the four-photon ionization comes from transitions with $\Delta l = +1$, but with no definite Δm required. Circular polarization can be just as effective as plane polarization.

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[2]C. S. Chang and P. Stehle, Phys. Rev. A 4, 641 (1971). Hereafter quoted as I.

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[4]The numerical values given in (10)–(14) are computed from the tables by D. R. Bates and A. Damgaard, Phil. Trans. Roy. Soc. London 242, 101 (1949), and P. M. Stone, Phys. Rev. 127, 1151 (1962). The number in (11) is also computed by B. A. Zon, M. L. Manakov, and L. P. Rapoport, Zh. Eksp. Teor. Fiz. 60, 1246 (1971) [Sov. Phys. JETP 33, 683 (1971)], using the quantum defect method.

[5]See, e.g., N. F. Ramsey, *Molecular Beams* (Oxford Univ. Press, Oxford, England, 1956); P. Kusch and V. W. Hughes, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1959), Vol. 37, Part I.

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