Computation of the ac Stark Effect in the Ground State of Atomic Hydrogen

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Using a Sturmian function expansion we have computed the nth-order coefficients $E_n(\omega)$, for $2 \leq n \leq 22$, in the perturbation expansion of the ac Stark effect in the hydrogen $1s$ state. An "effective convergence" similar to that in the dc case is observed. A parametrization of these coefficients, based upon the analytic structure of the Coulomb Green's function, separates the rapid oscillatory resonant behavior and the smooth background variation with respect to ω.

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The applicability of perturbation theory to the description of atomic systems in intense laser fields (intensity $I > 10^{13}$ W cm^{-2}) is a subject of continuing concern. Substantive arguments have been advanced[1] that perturbative treatments are inadequate for the analysis of the current generation of experiments on multiphoton ionization of atoms. These arguments have been robbed of much of their force by an analysis[2] of the effects of time evolution of the laser pulse, which indicates that, for pulse rise times longer than $\sim 10^{-13}$ s, the ionization stage of the atom increases with laser intensity so as to maintain the validity of perturbative description. The results of more recent experiments with subpicosecond pulses have been interpreted[3] in terms of field-shifted atomic resonances, a picture which suggests the important role of the atomic structures in spite of the influence of the intense field. Therefore, some form of perturbation theory based on a zeroth-order atomic system coupled with a radiation field may be appropriate. However, all these discussions have taken place without extensive reference to quantitative calculations, for few actual computations of high-order processes (photon number $n > 2$) can be found in the literature.[4] We are developing a method for such calculations in atomic hydrogen, and report here some initial results: nth-order frequency-dependent level shifts $E_n(\omega)$ of the ground state, for $n \leq 22$.

We proceed from standard expressions of perturbation theory. Let $H_0 = H_{\text{atom}} + H_{\text{rad}} = -\frac{1}{2}\nabla^2 - r^{-1} + \omega a^\dagger a$ be the zeroth-order Hamiltonian (in a.u.) for a hydrogen atom in a radiation field of frequency ω, and let $V = \mathbf{r}\cdot\mathbf{F}$ be the interaction that is treated perturbatively, with $\mathbf{F} = i(2\pi\omega/L^3)^{1/2}\hat{\boldsymbol{\epsilon}}(a - a^\dagger)$ the electric field operator. We treat the case in which the radiation field is linearly polarized. The zeroth-order eigenstate is $|\Psi_0\rangle = |\phi_{0,0}(\mathbf{r})\rangle|N\rangle$, where $\phi_{0,0}(\mathbf{r}) \equiv \pi^{-1/2}e^{-r}$ is the $1s$ state of hydrogen and N is the occupation number of the radiation field. The mth-order perturbed state Ψ_m is represented as

$$|\Psi_m\rangle = \sum_{k=-m}^{m} |\phi_{m,k}(\mathbf{r})\rangle|N-k\rangle, \tag{1}$$

where k runs in steps of 2. We require that $\langle\Psi_m|\Psi_0\rangle = \delta_{m0}$. The atomic wave functions $\phi_{m,k}(\mathbf{r})$ then satisfy the inhomogeneous equations

$$[E_0 + k\omega - H_{\text{atom}}]\phi_{m,k} = \mathbf{r}\cdot\hat{\boldsymbol{\epsilon}}(\phi_{m-1,k-1} + \phi_{m-1,k+1}) + \sum_{j=1}^{m/2} E_{2j}(\omega)\phi_{m-2j,k}, \tag{2a}$$

where the coefficients

$$E_{2m}(\omega) = \langle\Psi_m|\mathbf{r}\cdot\mathbf{F}/F|\Psi_{m-1}\rangle + \sum_{i=1}^{m}\sum_{j=1}^{m-1} E_{2m-i-j}(\omega)\langle\Psi_i|\Psi_j\rangle \tag{2b}$$

are the $2m$th-order coefficients in the Rayleigh-Schrödinger expansion for the energy of the atom:

$$E(\omega) = E_0 + \sum_{m=1}^{\infty} E_{2m}(\omega)F^{2m}, \quad E_0 = -\tfrac{1}{2}. \tag{3}$$

We have assumed that the intensity is high enough so we can neglect the depletion of the photon field and define the classical field amplitude as $F = (8\pi N\omega/L^3)^{1/2}$. Equation (2b) is derived by use of the remainder theorem,[5] which enables one to determine the $2m$th-order energy from the perturbed wave functions of order $\leq m$.

Following Dalgarno and Lewis,[6] we regard Eq. (2a) as a differential equation to be solved in its own right, without explicit reference to the spectrum of the unperturbed atom. This outlook has been adopted previously by Gontier and Trahin,[7] who have numerically integrated the differential equations. Our approach to the solution is to expand the $\phi_{m,k}$ in a basis of Sturmian functions:

$$\phi_{m,k}(\mathbf{r}) = r^{-1} \sum_{l=l_{\min}}^{m} \sum_{n=l+1}^{N_s} A_{m,k}^{nl} S_{nl}^{(\zeta)}(r) Y_{l0}(\hat{\mathbf{r}} \cdot \hat{\boldsymbol{\epsilon}}) , \quad (4)$$

where the Sturmian radial functions $S_{nl}^{(\zeta)}(r)$ are as defined in Ref. 8:

$$S_{nl}^{(\zeta)}(r) = \left[\frac{(n-l-1)!}{2(n+l)!} \right]^{1/2} (\zeta r)^{l+1} e^{-\zeta r/2} \times L_{n-l-1}^{(2l+1)}(\zeta r) , \quad (5)$$

and $l_{\min} = 0$ or 1 for m = even or odd. Substitution of (4) into (2a) yields, for each value of l, a separate set of linear equations that can be solved for the coefficients $A_{m,k}^{nl}$, for $n = l+1, \ldots, N_s$.

The Sturmian functions have several useful properties. They provide a denumerable basis set that is complete with respect to square integrable functions. On the other hand, they resemble the radial eigenfunctions $P_{nl}(r)$ of the bound states of hydrogen: when the parameter $\zeta = 2/n$, $S_{nl}^{(\zeta)}(r) = (n/\sqrt{2}) P_{nl}(r)$. Thus ζ can be chosen so that all states of hydrogen with a given principal quantum number are represented exactly within the Sturmian basis; alternatively, ζ can be chosen to give certain of the $\phi_{m,k}$ the correct exponential behavior at large r: $\zeta = 2/(1-2k\omega)^{1/2}$. The matrix elements of all operators in Eqs. (2) are simple functions of n and l (i.e., square roots of polynomials of degree ≤ 4), and they are banded by the selection rule $|\Delta n| \leq 2$ (and, trivially, $\Delta l = \pm 1$ for the electric dipole operator). This banded structure greatly facilitates the inversion of large matrices. Finally, a truncated Sturmian basis yields the *exact* solution to Eqs. (2) in the dc limit ($\omega \to 0$), for $\zeta = 2$. We have used this fact to check the stability of our numerical algorithms, and have computed $E_m(\omega = 0)$ for m up to 200. The results agree to all digits cited in previous calculations (for $m \sim 50$),[9] and agree with known asymptotic formulas.[10,11] We are restricted in the present treatment to cases in which the $\phi_{m,k}$ are L^2 functions, which implies that $\omega k < |E_0|$, the ionization limit.

In the results presented here, the number N_S of Sturmian basis functions for each value of l is 200. This number is determined by qualitative observations of convergence and stability, as is the value of ζ, which ranges between 2 and 0.5. Our computations are carried out on the CYBER 205 computer at the National Institute of Standards and Technology. Less than 5 s of central processor unit time is required to compute E_{22}, from perturbed wave functions of up to 11th order.

In Table I, we give the calculated energy coefficients for the fundamental frequency of a Nd-doped yttrium-

TABLE I. Energy coefficients, E_n, as defined in Eq. (3), for the hydrogen 1s state. The coefficients of the dc case are multiplied by a factor f_n, defined as $f_{2m} = (2m)!/[(m!)^2 2^{2m}]$. Numbers in parentheses show powers of ten.

Order n	dc	$\lambda = 1064$ nm	$\lambda = 533$ nm
2	−1.125 000	−1.137 437	−1.176 631
4	−2.083 008 (1)	−2.241 173 (1)	−2.840 897 (1)
6	−1.533 679 (3)	−1.894 898 (3)	−4.094 904 (3)
8	−2.171 742 (5)	−3.397 329 (5)	−2.762 216 (6)
10	−4.787 310 (7)	−1.076 252 (8)	−9.404 516 (9)
12	−1.494 801 (10)	−5.711 314 (10)	
14	−6.268 458 (12)	−5.119 799 (13)	
16	−3.406 609 (15)	−8.330 576 (16)	
18	−2.335 214 (18)	−2.543 771 (20)	
20	−1.975 272 (21)	−2.533 150 (24)	
22	−2.023 907 (24)	−1.807 757 (29)	

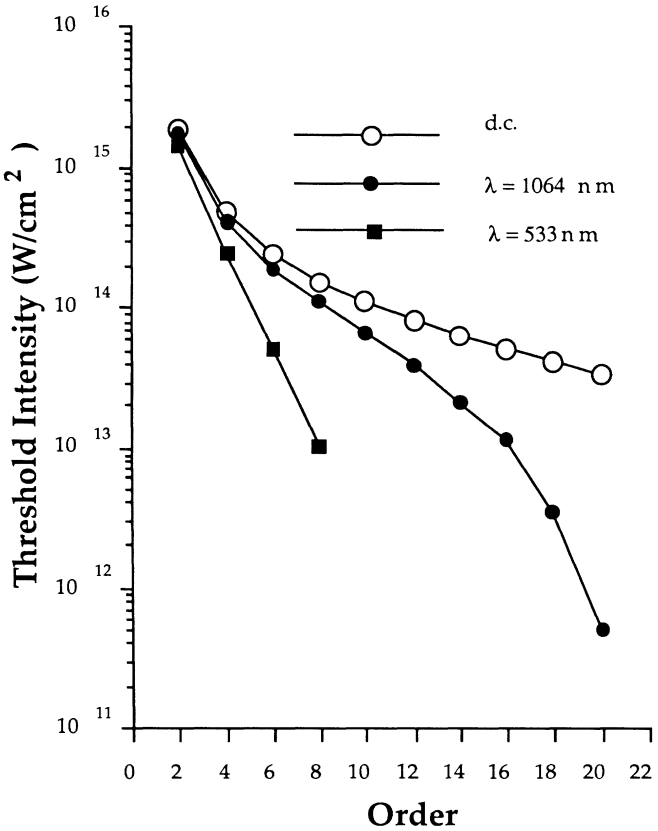

FIG. 1. The threshold intensity for each order of perturbation as determined by $I_{2m} = 3.5 \times 10^{16} E_{2m}/E_{2m+2}$. The threshold intensity for the dc case is defined, for the sake of comparison, as $I_{2m} = 3.5 \times 10^{16} E_{2m} f_{2m}/E_{2m+2} f_{2m+2}$ and the scaling factor is $f_{2m} = (2m)!/[(m!)^2 2^{2m}]$.

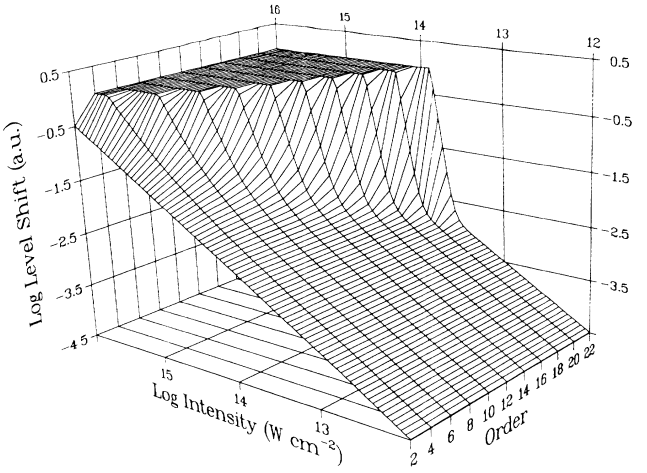

FIG. 2. The magnitude of the level shift of H 1s is computed by perturbation theory up to nth order, $\Delta E_n = |\sum_{k=1}^{[n/2]} E_{2k}(\omega) F^{2k}|$, for $\omega = 0.043$ a.u. (the Nd:YAlG frequency), as a function of the light intensity I in W cm^{-2}, for $n \leq 22$. The surface is arbitrarily truncated for $\Delta E_n > 1$ a.u. It is evident that for $I < 10^{14}$ perturbation theory exhibits "effective convergence" as discussed for the dc case in Ref. 11.

aluminum-garnet (Nd:YAlG) laser and its second harmonic, including the dc case as a comparison. In Fig. 1, we plot the "threshold intensity" versus the order of perturbation for these three cases. This threshold intensity corresponds to the square of field strength determined by $F^2(\text{a.u.}) = E_n/E_{n+2}$: it is the intensity at which the $(n+2)$th-order shift becomes equal to the nth. This result is of practical interest in indicating the range of intensities within which the level shifts of ground-state atoms may be adequately described by low-order perturbation theory. Our calculation indicates that, for the frequency of a Nd:YAlG laser the threshold intensity for the second-order perturbation is 1.77×10^{15} W/cm^2. At that intensity, the perturbation series diverges rapidly with increasing order.

It is well known[11] that the Rayleigh-Schrödinger perturbation expansion of the dc Stark is asymptotic: Although the series is divergent, its finite partial sums approximate the exact result in weak fields. On the other hand, there exists a proof that in the ac case the expansion converges,[12] though the radius of convergence is unknown. Our results for the first 22 terms of the expansion show behavior similar to that of the divergent dc case. Figure 2 shows the contribution of the first n terms in the perturbation expansion at the Nd:YAlG frequency, for $2 \leq n \leq 22$, in the intensity range $10^{12} \leq I \leq 10^{16}$ W/cm^2. The range of n covers all orders for which the level shift is real: Twelve-photon absorption ionizes H 1s, so that the 24th-order level shift has an imaginary part. For intensities below the baseline of the "butte" in this figure the level shift shows an "effective convergence" similar to that encountered in the dc case,[11] and we therefore advance the conjecture that for $I < 10^{14}$ W/cm^2 the partial sum is a good approximation to the exact level shift. This conjecture remains to be tested by the nonperturbative calculations, such as done by the rotated coordinate method,[4] or by experimental determination of the level shift. The asymptotic limit $(n \to \infty)$ of this baseline determines the radius of convergence of perturbation theory. We do not know how the higher-order complex coefficients will behave, but naive extrapolation of this baseline would give a radius of convergence corresponding to $I \sim 10^{12}$ W/cm^2.

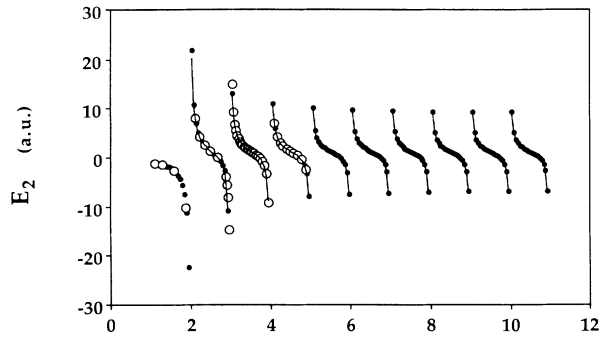

FIG. 3. The second-order energy coefficient, E_2, as a function of laser frequency, on the scale of effective principal quantum number $\nu = (1-2\omega)^{-1/2}$. The dots represent the results of our calculation. The circles are the results from Ref. 13, included as a comparison. The line is obtained from the equation and the parameters in Table II.

Systematic study of the ac level shift is complicated by the strong frequency dependence of the coefficients. This dependence is greatly simplified by plotting $E_{2n}(\omega)$ as a

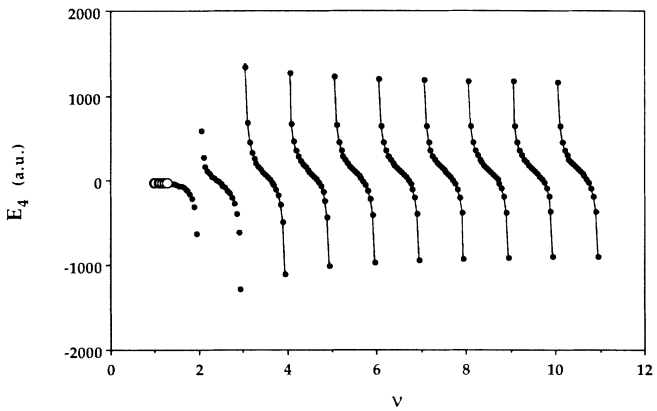

FIG. 4. The fourth-order energy coefficient, E_4, as a function of laser frequency, on the scale of effective principal quantum number $\nu = (1-4\omega)^{-1/2}$. The dots represent the results of our calculation. The circles, which lie too close to resolve, represent the results from Ref. 14, included as a comparison. The line is obtained from the equation and the parameters in Table II.

TABLE II. Asymptotic parameters for E_2, E_4, and E_6 from nonlinear fitting. In the asymptotic region $\epsilon \to 0$, E_{2n} can be reproduced by $E_{2n} = a_0 + a_1\epsilon + a_2\epsilon^2 + (b_0 + b_1\epsilon + b_2\epsilon^2)\cot(\pi\nu)$.

Parameter	E_2	E_4	E_6
a_0	1.077552	1.379988 (2)	3.013495 (4)
a_1	−2.525347	1.275521 (3)	1.094091 (6)
a_2	−4.571427	−8.393799 (3)	1.076715 (7)
b_0	1.227783	1.598350 (2)	4.378240 (4)
b_1	−8.901760	−8.934785 (2)	5.027776 (5)
b_2	4.923770 (1)	1.166016 (3)	1.879651 (6)
Fitting range	$4 < \nu < 11$	$5 < \nu < 11$	$5 < \nu < 11$

function of $\nu = (1 - 2n\omega)^{-1/2}$, which is the effective principal quantum number of the highest virtual state reached in the n-photon absorption process. The coefficients E_2 and E_4 then exhibit the periodicity of a cotangent function, as shown in Figs. 3 and 4. This behavior has been derived for $n = 1$ by Khristenko and Vechinkin,[13] from an asymptotic development of their closed-form expression for E_2. Closed-form expressions are unknown for $n > 1$; however, we find that the essential result can be generalized by considering the analytic structure of the energy-dependent Coulomb Green's function $G_\epsilon(r,r')$. This structure has been discussed in some detail by Greene, Fano, and Strinati.[15] Following their notation, we find that, for $\epsilon = -1/(2\nu^2) = -\frac{1}{2} + n\omega < 0$, $G_\epsilon(r,r')$ can be rewritten as

$$G_\epsilon(r,r') = \pi f^0(r_<) g^0(r_>) + \pi[\mathcal{G}(\epsilon) + A(\epsilon)\cot(\pi\nu)] f^0(r) f^0(r') , \quad (6)$$

where the functions f^0, g^0, $\mathcal{G}(\epsilon)$, and $A(\epsilon)$ are analytic as $\epsilon \to 0$. Details of the Green's function expansion for $E_{2n}(\omega)$ can be found in Refs. 14 and 16. We consider here the case in which resonances occur only in n-photon absorption. In this case, there is only one singular term in that expansion, which can be expressed as $\langle \Psi_0 | V G_\epsilon(r,r') V W | \Psi_0 \rangle$, where W is a $(2n-2)$-fold operator product of V and Green's functions with energies $\epsilon' < \epsilon$. Equation (6) then implies that

$$E_{2n}(\omega) = a_{2n}(\epsilon) + b_{2n}(\epsilon)\cot(\pi\nu) , \quad (7)$$

where $a_{2n}(\epsilon)$ and $b_{2n}(\epsilon)$ are analytic functions of ϵ near $\epsilon = 0$. We have therefore fitted our computed energy coefficients with the form (7), taking a_{2n} and b_{2n} to be polynomials in ϵ of degree 2. The results, shown in Table II, can be used to reproduce the second-, fourth-, and sixth-order energies quite accurately over the asymptotic region and to extrapolate these quantities all the way to the ionization limit. Extension of this approach to higher orders is straightforward, though intermediate resonances introduce additional frequency dependence.

In conclusion, we have carried out calculations of the nth-order ac level shift of H $1s$ for $n > 20$. These results provide the first quantitative evidence for effective convergence of perturbation theory. Fits with analytic formulas permit the coefficients to be represented efficiently over a wide range of photon frequency.

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