

## Calculation of multiphoton-ionization Green's functions using the Wentzel-Kramers-Brillouin approximation. II

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(Received 10 June 1992)

Recently, a technique [M. Edwards, *Phys. Rev. A* **45**, 409 (1992)] was presented for calculating multiphoton-ionization Green's functions based on the Wentzel-Kramers-Brillouin (WKB) approximation. In that paper it was shown that the ability of this method to produce accurate cross sections and angular distributions depended critically on the single-particle potential for the valence electron that was used in the calculation. In this work we present a supporting technique for determining the optimal potential for use with this method in low- $Z$  alkali-metal atoms. The technique produces the parameter values for a parametric model potential whose WKB Green's function has poles that coincide with the measured energy levels of the atom. We have determined the parameter values for a specific model potential in Li and Na. For these cases, only two parameters are needed to produce a potential whose WKB energy levels match all of the measured ones to within  $165 \text{ cm}^{-1}$ . We have calculated cross sections for two-photon ionization of Li and Na for a range of laser-photon energies using this model potential and present comparisons with previous work.

PACS number(s): 32.80.Rm, 42.50.Hz

### I. INTRODUCTION

Although lowest-order perturbation theory (LOPT) is not valid for the type of multiphoton processes that have been the main focus of research for the past several years (e.g., multiphoton ionization with ultrahigh-intensity, ultrashort pulsed lasers), its importance has not diminished. Non-perturbative dynamical models of these processes usually include atomic parameters such as  $n$ -photon Rabi frequencies and ac-Stark shifts [2]. The quantitative and even qualitative predictions of such dynamical models are often sensitive to the actual values of these quantities. And since they are many times calculated perturbatively, LOPT continues to play a role in these models.

The LOPT expression for multiphoton-ionization cross sections and angular distributions (as well as the atomic parameters mentioned above) generally take the form of sums over complete sets of atomic states divided by energy-level differences. These cross sections exhibit a rapidly varying dependence on the energy of the laser photon. The value of the cross section near a minimum depends sensitively on all terms in the summation and also on the accuracy of the wave functions used.

The practical problem of extracting numerical values from such expressions generally divides into two parts. First, accurate atomic wave functions are required; and second, a method for performing the infinite summations over the complete set of atomic sets (both bound and continuum) is needed. Many of the methods used in the past have balanced these two requirements.

Other methods have included the truncated-summation method [3], the Dalgarno-Lewis technique [4], and the Green's-function method [5]. In the Green's-function method, the summation is converted to an  $N$ -dimensional integral (where  $N$  is the order of the multiphoton process) with the Green's functions replac-

ing the infinite summations. This method has the advantage of accounting for the entire sum, both the bound and continuum parts. Evaluation of the Green's function was initially done only for cases in which the atomic wave functions were known exactly [6] or within the framework of quantum defect theory [7].

Recently a method for approximating the Green's functions based on the WKB method was introduced [1]. In that work it was shown that all of the functions appearing in the integrand of the  $N$ -photon radial matrix element needed for calculating cross sections and angular distributions satisfied a differential equation of the same form. The solutions of differential equations of that form could be approximated using the WKB method. This allowed all of the functions appearing in the matrix element to be uniformly approximated.

The WKB method has an important advantage over the single-channel quantum defect theory (QDT) method for this type of calculation. The WKB method wave functions behave correctly near the origin. The QDT continuum state wave function, however, diverges in this region requiring that a cutoff function be inserted so that the  $N$ -photon radial matrix element will not diverge. Also, if the region near the origin contributes appreciably to the matrix element, the accuracy of the QDT result will be degraded. This does not appear to necessarily be the case with the WKB method.

Although the WKB Green's-function method has been applied to the calculation of multiphoton-ionization cross sections, it is in principle applicable to any expression that has the form of sums of matrix elements divided by energy-level differences, provided that the summations extend over a complete set of states. Sums of this form occur in the general Rayleigh-Schrödinger perturbation expansion. This indicates that the method can be used to calculate a wide range of quantities.

As was noted in the previous paper [1] (hereinafter referred to as ME), the potential used for the outermost electron is of critical importance in the performance of the WKB method in alkali-metal atoms. In order to obtain accurate estimates of multiphoton-ionization cross sections with this method, the poles of the WKB Green's function must be positioned correctly. Therefore a technique for the determination of such a potential represents a critical element in the overall procedure. A candidate technique is presented in this paper.

In Sec. II we present the condition that determines the positions of the poles of the WKB-approximate Green's function. Then we describe a general technique for determining the values of the parameters in a parametric single-electron model potential. No specific mathematical form is assumed for the model potential in the general technique. In Sec. III this technique is applied to Li and Na for a particular model potential. In Sec. IV we present two-photon ionizations cross sections in Li and Na where we have used the previously determined model potential and then compare these cross sections with previous calculations.

## II. GENERAL TECHNIQUE

### A. WKB Green's-function method

The basic quantity that must be calculated in estimating multiphoton-ionization cross sections and angular distributions is [8]

$$M_{\nu_N \dots \nu_0} = \int_0^\infty dr_N \dots \int_0^\infty dr_1 u_{\nu_N}(r_N) r_N \times g_{\nu_{N-1}}(r_N, r_{N-1}) \dots \times r_1 u_{\nu_0}(r_1), \quad (1)$$

the  $N$ -photon radial matrix element of LOPT. In the above equation  $\nu_n = (E_n, l_n)$ ,  $E_n = E_0 + n\hbar\omega$  ( $E_0$  is the energy of the initial atomic state),  $\omega$  is the laser-photon frequency, and  $l_n$  is the angular momentum of the set of intermediate states reached by the absorption of  $n$  photons. The quantities  $u_{\nu_N}(r)$  and  $u_{\nu_0}(r)$  are the radial parts of the final continuum- and initial-state wave functions, respectively. The factor  $g_\nu(r, r')$  is the radial Green's function which may be written as [1]

$$g_\nu(r, r') = -2\pi R_\nu(r_<) I_\nu(r_>). \quad (2)$$

As noted in ME, all of the functions appearing in the integrand of Eq. (1),  $u_{\nu_N}(r)$ ,  $u_{\nu_0}(r)$ ,  $R_\nu(r)$ , and  $I_\nu(r)$ , satisfy a differential equation of the form

$$(E - H_\nu)\psi_\nu = 0, \quad (3)$$

where  $\nu = (E, l)$ . We use atomic units throughout the rest of this paper except as explicitly noted. The radial Hamiltonian  $H_\nu$  has the form

$$H_\nu = -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + U(r), \quad (4)$$

where the function  $U(r)$  is the full potential energy of the electron.

The WKB method can then be applied to Eq. (3). The WKB general solution has different forms for different intervals of the radial coordinate  $r$ . The end points of these intervals are roughly determined by the positions of the turning points of the classical motion of an electron having a potential energy  $U(r)$ . Solutions in regions far from the turning points are called "proper solutions" and are given by the standard WKB approximation solutions [9]. Solutions valid near a turning point are called "local solutions." These solutions are determined by approximating the effective potential energy  $[U(r) + l(l+1)/2r^2]$  near the turning point to first order in  $r$  (linear turning points) and solving the approximate differential equation.

The typical turning point structure of electron potentials in low- $Z$  alkali-metal atoms consists of two "well-spaced," linear turning points. Turning points are termed "well-spaced" when their separation is larger than or comparable to the size of the region of validity of the local solutions.

Approximations for the specific functions appearing in Eq. (1) from the WKB general solutions are obtained by imposing continuity boundary conditions between adjoining proper and local solutions and by imposing specific boundary conditions for each function at  $r=0$  and  $\infty$ . Such solutions were obtained for two well-spaced, linear turning points ( $E < 0$ ) and for one linear turning point ( $E > 0$ ) in ME.

The WKB solutions for  $E < 0$  where there are two turning points consist of different forms in each of five regions of the radial coordinate. Two of the five regions surround the turning points (the region around the inner turning point is labeled A and that around the outer turning point is labeled B) and the local solutions are valid in these regions. The other three regions are those in which the proper solutions are valid. They are labeled I for  $r$  smaller than the inner turning point, II for  $r$  between the turning points, and III for  $r$  greater than the outer turning point.

### B. Positions of the WKB Green's-function poles

As a result of boundary condition matching, the WKB Green's-function regular part  $[R_\nu(r)]$  and irregular part  $[I_\nu(r)]$  are given by [1], for  $E < 0$ ,

$$R_\nu^{(I)}(r) = \frac{(2/\pi)^{1/2} e^{-i\theta_\nu}}{4 \cos(\alpha_\nu)} |C_\nu(r)|^{-1/2} \exp[-|w_\nu(r)|], \quad (5)$$

$$I_\nu^{(I)}(r) = (2/\pi)^{1/2} e^{i\theta_\nu} \cos(\alpha_\nu) |C_\nu(r)|^{-1/2} \exp[|w_\nu(r)|], \quad (6)$$

$$R_\nu^{(A)}(r) = \frac{e^{-i\theta_\nu}}{4 \cos(\pi/6) \cos(\alpha_\nu)} [w_\nu(r)/C_\nu(r)]^{1/2} \times [J_{1/3}(w_\nu(r)) + J_{-1/3}(w_\nu(r))], \quad (7)$$

$$I_v^{(A)}(r) = \frac{e^{i\theta_v} [w_v(r)/C_v(r)]^{1/2}}{\cos(\pi/6)} \times \left[ \sin \left[ \alpha_v - \frac{\pi}{3} \right] J_{1/3}(w_v(r)) + \sin \left[ \alpha_v - \frac{2\pi}{3} \right] J_{-1/3}(w_v(r)) \right], \quad (8)$$

$$R_v^{(II)}(r) = \frac{(2/\pi)^{1/2} e^{-i\theta_v}}{2 \cos(\alpha_v)} |C_v(r)|^{-1/2} \cos \left[ w_v(r) - \frac{\pi}{4} \right], \quad (9)$$

$$I_v^{(II)}(r) = (2/\pi)^{1/2} e^{i\theta_v} |C_v(r)|^{-1/2} \cos \left[ w_v(r) - \alpha_v + \frac{\pi}{4} \right], \quad (10)$$

$$R_v^{(B)}(r) = \frac{e^{-i\theta_v} [w'_v(r)/C_v(r)]^{1/2}}{2 \cos(\pi/6) \cos(\alpha_v)} \times \left[ \sin \left[ \alpha_v - \frac{\pi}{3} \right] J_{1/3}(w'_v(r)) + \sin \left[ \alpha_v - \frac{2\pi}{3} \right] J_{-1/3}(w'_v(r)) \right], \quad (11)$$

$$I_v^{(B)}(r) = \frac{e^{i\theta_v} [w'_v(r)/C_v(r)]^{1/2}}{2 \cos(\pi/6)} \times [J_{1/3}(w'_v(r)) + J_{-1/3}(w'_v(r))], \quad (12)$$

$$R_v^{(III)}(r) = \frac{1}{2} (2/\pi)^{1/2} e^{-i\pi/4} |C_v(r)|^{-1/2} \times \left\{ \exp \left[ |w'_v(r)| - i \left[ \theta_v - \frac{\pi}{4} \right] \right] + \exp \left[ -|w'_v(r)| + i \left[ \theta_v - \frac{\pi}{4} \right] \right] \right\}, \quad (13)$$

$$I_v^{(III)}(r) = \frac{1}{2} (2/\pi)^{1/2} e^{i\theta_v} |C_v(r)|^{-1/2} \exp[-|w'_v(r)|], \quad (14)$$

where

$$C_v(r)^2 = 2 \left\{ E - \left[ U(r) + \frac{(l + \frac{1}{2})^2}{2r^2} \right] \right\}, \quad (15)$$

$$w_v(r) = \int_{r_0}^r C_v(r') dr', \quad (16)$$

$$w'_v(r) = \int_r^{r_1} C_v(r') dr', \quad (17)$$

$$\theta_v = \sigma_v - \alpha_v, \quad (18)$$

$$\sigma_v = \lim_{r \rightarrow \infty} \left\{ w_v^{(c)}(r) + \frac{\pi}{4} - \left[ kr - \frac{1}{2} l\pi + \frac{1}{k} \ln(2kr) \right] \right\}, \quad (19)$$

$$\alpha_v = \int_{r_0}^{r_1} C_v(r') dr', \quad (20)$$

and  $k = (2E)^{1/2}$ . The functions  $J_{\pm 1/3}(x)$  are Bessel functions of order  $\pm \frac{1}{3}$ .

In the above equations,  $r_0$  and  $r_1$  are the inner and outer turning points associated with  $U(r)$  and the energy  $E$ . Also  $w_v^{(c)}(r)$  is a special case of  $w_v(r)$  given in Eq. (16) where  $U(r')$  is replaced by the Coulomb potential energy.

By examining Eqs. (5)–(14) it is easy to find the condition that determines the positions of the poles of the WKB Green's function. Note that, for all values of  $r$  except in region III,  $R_v(r)$  is inversely proportional to  $\cos(\alpha_v)$  while  $I_v(r)$  is directly proportional to this quantity only in region I. Thus at values of  $E$  for which  $\cos(\alpha_v)$  is equal to zero the WKB Green's function will diverge.

This condition on  $E$  can be written as

$$\alpha_v = \int_{r_0}^{r_1} C_v(r') dr' = (n' + \frac{1}{2})\pi = (n - l - \frac{1}{2})\pi, \quad (21)$$

where  $n'$  is the number of nodes in the radial wave function and  $n$  and  $l$  are the usual principal and angular momentum quantum numbers, respectively. This is precisely the well-known [9] condition that determines the energy levels of bound states of  $U(r)$  under the WKB approximation for the case of two linear, well-spaced turning points. Thus we have the intuitive result that the poles of the WKB Green's function occur at the positions of the WKB energy levels.

These poles also correspond to the positions of the resonances in the  $N$ -photon ionizations cross section. The  $N$ -photon radial matrix element given in Eq. (1) contains  $N-1$  Green's functions  $g_v(r, r')$ . The  $n$ th of these functions represents the intermediate summation associated with the absorption of the  $n$ th photon. This Green's function is evaluated at an energy  $E_n = E_0 + n\omega$ , where  $\omega$  is the energy of the laser photon. When the laser is tuned so that  $E_n$  coincides with one of the energies determined by Eq. (21), the  $N$ -photon radial matrix element (and hence the cross section) diverges. This is manifested as a LOPT cross-section resonance.

Since multiphoton-ionization cross sections vary rapidly with photon energy, it is important that the poles of the WKB Green's function be correctly positioned. As seen above, this will occur if the WKB bound-state energy levels coincide with the measured levels. It is possible to develop a numerical technique based on Eq. (21) whose WKB bound-state energy levels are equal to the measured ones. Such a technique is presented below.

### C. Technique

#### for determining model potential parameter values

The general method for determining the parameter values in a parametric model potential may be formulated without reference to any specific mathematical form for the potential. We assume that the electron potential energy  $U$  depends on  $M$  fitting parameters,

$$U(r, x_1, x_2, \dots, x_M) \equiv U(r, \mathbf{x}), \quad (22)$$

where  $\mathbf{x}$  is a column vector whose elements are the fitting parameters

$$\mathbf{x} = \begin{bmatrix} x_1 \\ \vdots \\ x_M \end{bmatrix}. \quad (23)$$

Here  $M$  is the number of energy levels we wish to fit. We denote these levels  $E_{n_1 l_1}^{(e)}, E_{n_2 l_2}^{(e)}, \dots, E_{n_M l_M}^{(e)}$ . For producing accurate multiphoton-ionization cross sections, it is essential that one of these levels be the ground state.

$$f_i(E_{n_i l_i}^{(e)}, n_i, l_i, \mathbf{x}) \equiv \int_{r_0}^{r_1} \left\{ 2 \left[ E_{n_i l_i}^{(e)} - \left( U(r, \mathbf{x}) + \frac{(l_i + \frac{1}{2})^2}{2r^2} \right) \right] \right\}^{1/2} dr - (n_i - l_i - \frac{1}{2})\pi = 0, \quad (24)$$

where  $i = 1, \dots, M$ . The turning points  $r_0$  and  $r_1$  are themselves functions of  $E_{n_i l_i}^{(e)}$ ,  $l_i$ , and  $\mathbf{x}$  and are determined by the following conditions:

$$E_{n_i l_i}^{(e)} - \left[ U(r_0, \mathbf{x}) + \frac{(l_i + \frac{1}{2})^2}{2r_0^2} \right] = 0 \quad (25)$$

and

$$E_{n_i l_i}^{(e)} - \left[ U(r_1, \mathbf{x}) + \frac{(l_i + \frac{1}{2})^2}{2r_1^2} \right] = 0. \quad (26)$$

Note that there is a different pair of turning points for each experimental energy.

The condition that all of the functions  $f_i$  equal zero constitutes a set of  $M$  nonlinear equations that determines the parameters  $x_1, x_2, \dots, x_M$ . In general, these equations must be solved numerically. We have chosen the well-known Newton-Raphson method [10] for their solution.

The Newton-Raphson algorithm is an iterative method

$$\frac{\partial f_i}{\partial x_j} = - \int_{r_0}^{r_1} \left[ \frac{\partial U}{\partial x_j} \right] \left\{ 2 \left[ E_{n_i l_i}^{(e)} - \left( U(r, \mathbf{x}) + \frac{(l_i + \frac{1}{2})^2}{2r^2} \right) \right] \right\}^{-1/2} dr, \quad (30)$$

since the integrand of Eq. (24) vanishes at both  $r_0$  and  $r_1$ .

For the purpose of calculating multiphoton-ionization cross sections for a restricted range of laser-photon energies, it is possible to fit only a few energy levels to produce satisfactory results. These levels could be the ground state and only those levels that are scanned across in the energy range of interest. For a high-order multiphoton process, the number of resonances in the range can become large. Fitting this many levels such that the poles of the WKB Green's function are very accurately positioned using the above technique becomes a highly numeric-intensive task.

For low- $Z$  alkali-metal atoms, however, it is possible to fit all of the tabulated energy levels with reasonable accuracy using only two fitting parameters. In the next section, we apply the above procedure to fit the lowest two levels of Li and Na. We also illustrate with this example that reasonable initial estimates for the fitting parameters may be obtained if the physical meanings of these parameters are known. If these estimates are not sufficiently close to the actual solutions, the iterative Newton-Raphson method may not converge.

To obtain the equations that determine the values of the fitting parameters,  $x_k$ , we insert each experimental energy level into the integral in Eq. (21) to get

that requires an initial estimate,  $\mathbf{x}_0$ , to converge to a solution. The  $(n+1)$ th approximation to the solution is expressed in terms of the  $n$ th approximation by the following equation:

$$\mathbf{x}_{n+1} = \mathbf{x}_n - A^{-1}(\mathbf{x}_n) \mathbf{f}(\mathbf{x}_n), \quad (27)$$

where  $\mathbf{f}(\mathbf{x})$  is a vector whose elements are the  $f_i(E_{n_i l_i}^{(e)}, n_i, l_i, \mathbf{x})$ ,

$$\mathbf{f}(\mathbf{x}) = \begin{bmatrix} f_1(E_{n_1 l_1}^{(e)}, n_1, l_1, \mathbf{x}) \\ \vdots \\ f_M(E_{n_M l_M}^{(e)}, n_M, l_M, \mathbf{x}) \end{bmatrix}. \quad (28)$$

The quantity  $A$  is the matrix of partial derivatives of  $\mathbf{f}(\mathbf{x})$  given by

$$A_{ij}(\mathbf{x}_n) = \left[ \frac{\partial f_i}{\partial x_j} \right]_{\mathbf{x}=\mathbf{x}_n}. \quad (29)$$

The partial derivative can be written as

### III. TWO-PARAMETER FITS FOR Li AND Na

We have chosen a screened Coulomb parametric model potential

$$U(r, \mathbf{x}) = - \frac{Z_{\text{eff}}(r, \mathbf{x})}{r}, \quad (31)$$

where

$$Z_{\text{eff}}(r, \mathbf{x}) = Z - \sum_{k=1}^L \frac{L_k}{\{1 + \exp[-x_{2k-1}(r - x_{2k})]\}}. \quad (32)$$

This model potential imitates the shell structure of the atom. The function  $Z_{\text{eff}}(r, \mathbf{x})$  is the screening function for the valence electron. The core electrons are divided into  $L$  shells where the  $k$ th shell contains  $L_k$  electrons and is located at an average radius  $x_{2k}$  from the nucleus. The shell is assumed to have a spherical shape whose radial thickness is roughly equal to the reciprocal of the sharpness parameter  $x_{2k-1}$ . The total number of electrons in the core must be  $\sum_{k=1}^L L_k = Z - 1$  where  $Z$  is the atomic number of the atom. This ensures that  $U(r, \mathbf{x})$  behaves

correctly as  $r \rightarrow \infty$ .

There are many ways to partition the core electrons for use with this model potential. We have chosen the simplest possible partition: one shell containing  $Z - 1$  electrons. This reduces the number of parameters to two. The screening function then has the form

$$Z_{\text{eff}}(r, x_1, x_2) = Z - \frac{(Z - 1)}{\{1 + \exp[-x_1(r - x_2)]\}}. \quad (33)$$

To obtain initial estimates for the parameters  $x_1$  and  $x_2$  for Li we assumed that both  $1s$  core electrons were exposed to the full nuclear Coulomb potential. Their average distance from the nucleus is then given by [12]

$$\langle r \rangle_{nl} = \frac{1}{2Z_{nl}} [3n^2 - l(l + 1)], \quad (34)$$

where  $Z_{nl}$  is obtained by assuming that shells closer to the nucleus than  $nl$  completely screen the nuclear charge. For Li there is indeed only one shell in the core, thus  $Z_{1s} = Z = 3$ . This makes  $\langle r \rangle_{1s} = x_2 = 0.5$  a.u. For Na the initial distance parameter used was the average distance of the middle core shell ( $2s$ ) assuming that the  $2s$  electrons are fully screened by the  $1s$  shell so that  $Z_{1s}$  in Eq. (34) is 9 instead of 11. Thus  $\langle r \rangle_{2s} = x_2 = 0.67$  a.u. The functions  $f_i(E_{n_i, l_i}, n_i, l_i, \mathbf{x})$  vary much less rapidly when the sharpness parameter ( $x_1$ ) changes than when the average distance parameter ( $x_2$ ) is varied. Thus we have used 4.0 for the initial estimate in all cases. This makes the radial thickness of the shell roughly 0.25 a.u. The convergence or nonconvergence of the Newton-Raphson procedure is relatively insensitive to this choice.

We have used this model potential to fit the  $2s_{1/2}$  and  $2p_{1/2}$  levels of Li and the  $3s_{1/2}$  and  $3p_{1/2}$  levels of Na [11]. The values of the fitted parameters along with the final values of the  $f_i$  are given in Table I.

The model potentials produced by these fits have WKB energy-level spectra that agree quite well with all of the measured levels. Once the parameters in  $U(r, \mathbf{x})$  have been determined, the positions of the WKB energy levels for other  $nl$  values may be calculated by a Newton-Raphson method similar to that described above. Table II presents a comparison of the lowest 20 WKB energy

TABLE I. This table presents the results of fitting the model potential of Eqs. (31) and (33) to the two lowest levels of Li and Na. The second and third columns contain the final fitting parameter values  $x_1$  and  $x_2$  in a.u. for each atom. These parameters were determined by varying these parameters so that the functions defined in Eq. (24) were simultaneously zero. The level label and the final value of each function are given in the fourth and fifth columns. In the fifth column, the quantities in square brackets indicate the power of 10 by which the number preceding the brackets is multiplied.

Atom	$x_1$ (length a.u.) <sup>-1</sup>	$x_2$ (length a.u.)	$nl$	$f_{nl}$
Li	3.443 71	0.435 86	$2s$	+5.3[ -6]
			$2p$	-1.8[ -6]
Na	4.434 15	0.400 36	$3s$	-7.7[ -6]
			$3p$	-3.7[ -5]

levels with their measured values for both Li and Na. We find that the largest difference occurs in the  $np$  series of levels for both atoms. The maximum difference for any two levels is  $165 \text{ cm}^{-1}$ . For all but three levels the difference is less than  $50 \text{ cm}^{-1}$ .

#### IV. CROSS-SECTION RESULTS FOR Li AND Na

As a test of the usefulness of these model potentials for Li and Na, we have calculated two-photon ionization cross sections for these atoms for the case of linearly polarized laser light using the WKB Green's-function method. The two-photon radial integrals were calculated by a method identical to that described in ME. We briefly describe that method here.

For linearly polarized light, the two-photon ionization cross section can be written as [1]

$$\sigma_2^{(L)} = (8.069 \times 10^{-53}) E_{ph}^2 \left( \frac{1}{9} |M_{v_{20}v_1v_0}^{(2)}|^2 + \frac{4}{45} |M_{v_{22}v_1v_0}^{(2)}|^2 \right). \quad (35)$$

The quantities  $M_{v_{20}v_1v_0}^{(2)}$  and  $M_{v_{22}v_1v_0}^{(2)}$  are the two-photon

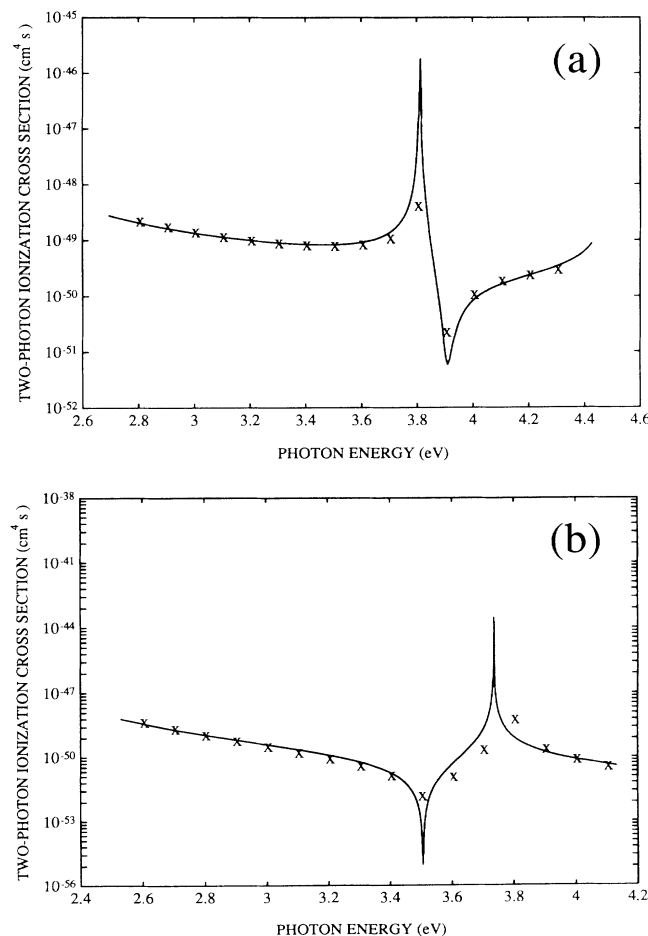


FIG. 1. (a) A plot of the two-photon ionization cross section around the  $3p$  resonance of Li vs photon energy. (b) A similar plot for Na around the  $4p$  resonance. The points marked with a  $x$  are the results of Ref. [13].

radial matrix elements that represent the two angular momentum pathways from the initial  $s$  bound state to the  $s$  and  $d$  partial wave continuum states, respectively. Each of these double integrals was written in the form of two integrals that could be converted into a system of differential equations. The differential systems were then evaluated numerically using a fourth-order Runge-Kutta algorithm. This method has been described in detail in a previous work [8].

For Li, two-photon ionization cross sections were calculated for photon energies ranging from 2.6 to 4.6 eV.

This range of energies scans across the  $3p$  resonance of Li. For Na, cross sections were calculated in a range of energies between 2.4 and 4.2 eV. This range scans across the  $4p$  resonance of Na. The results are presented in Figs. 1(a) for Li and 1(b) for Na.

We have chosen these ranges so that the results can be compared with those of Mizuno [13], who published cross-section results in tabular rather than graphical form. These points are marked with an  $x$  in Fig. 1 and were calculated by the Dalgarno-Lewis technique using a single-electron potential due to Bottcher [14]. The cross

TABLE II. This table presents a comparison of the lowest 20 WKB-approximate energy levels with the measured levels of Ref. [11] for a Li and (b) Na. The fourth column lists the difference between these two numbers. The first two levels listed were used to determine the values of the model parameters. Note that, for fixed angular momentum, the difference between levels of higher  $n$  decreases.

$nl$	$E_{nl}$ (Moore's tables) ( $\text{cm}^{-1}$ )	$E_{nl}$ (WKB) ( $\text{cm}^{-1}$ )	$E_{nl}$ (Moore's tables)- $E_{nl}$ (WKB) ( $\text{cm}^{-1}$ )
(a) Li			
2s	00 000.0	-0.09	+0.09 (fitted)
2p	14 903.66	14 903.68	-0.02 (fitted)
3s	27 206.12	27 219.81	-13.69
3p	30 925.38	30 760.26	+165.12
3d	31 283.08	31 294.14	-11.06
4s	35 012.06	35 017.75	-5.69
4p	36 469.55	36 383.06	+86.49
4d	36 623.38	36 628.57	-5.19
4f	36 630.20	36 628.60	+1.60
5s	38 299.50	38 302.25	-2.75
5p	39 015.56	38 968.00	+47.56
5d	39 094.93	39 097.66	-2.73
5f	39 104.50	39 097.70	+6.80
6s	39 987.64	39 989.14	-1.50
6p	40 390.84	40 362.78	+28.06
6d	40 437.31	40 438.91	-1.60
7s	40 967.90	40 968.92	-1.02
7p	41 217.35	41 199.32	+18.03
7d	41 246.50	41 247.63	-1.13
8s	41 587.10	41 588.02	-0.92
(b) Na			
3s	00 000.0	0.13	-0.13 (fitted)
3p	16 956.18	16 956.45	-0.27 (fitted)
4s	25 739.86	25 723.93	+15.93
3d	29 172.86	29 256.61	-83.75
4p	30 266.88	30 143.93	+122.95
5s	33 200.70	33 192.58	+8.12
4d	34 548.75	34 591.06	-42.31
4f	34 588.60	34 591.07	-2.47
5p	35 040.27	34 971.19	+69.08
6s	36 372.65	36 368.38	+4.27
5d	37 036.78	37 060.15	-23.37
5f	37 057.60	37 060.16	-2.56
5g	37 060.20	37 060.16	+0.04
6p	37 296.51	37 256.68	+39.83
7s	38 012.07	38 009.64	+2.43
6d	38 387.29	38 401.38	-14.09
6f	38 400.10	38 401.39	-1.29
6h	38 403.40	38 401.39	+2.01
7p	38 540.40	38 515.86	+24.54
8s	38 968.35	38 967.07	+1.28

sections have also been calculated by McGuire [15] where good agreement with Mizuno was obtained. Figure 1 shows that for both Li and Na the agreement between the present work and that of Mizuno is quite good. The positions of the resonances and the antiresonances in both graphs are offset by no more than 0.1 eV from those of Mizuno.

In conclusion, we showed that the poles of the WKB Green's function coincide with the WKB energy-level positions and presented a general technique for determining the parameter values for a parametric model potential whose WKB energy levels match the measured values. We also applied this technique for a specific model potential for the valence electrons of Li and Na. We found that, using only two parameters, all of the measured energy levels for these atoms could be fitted to within  $165 \text{ cm}^{-1}$ . We then used this model potential in the calculation of two-photon ionization cross sections in these atoms. We obtained good agreement with previous calculations of the same cross sections.

The technique of using the WKB energy-level conditions to determine the values of parameters in the model

potential is an integral part of the WKB Green's-function method. We have shown above that it is possible in some cases to reproduce an entire energy-level spectrum with a very few model parameters. Thus, unless tighter accuracy constraints are imposed on the Green's function, no further model potential fitting is required for such a case. If such accuracy is needed, it is possible to fit particular energy levels.

We have also seen that the resulting Green's function produces good results for cross sections. Thus it seems that the WKB Green's-function method, as described in this paper and in ME, promises to be a useful technique for the calculation of a wide range of quantities. Further study is needed, however, for refining the fitting technique described in this paper and also for extending and applying the method to other cases.

#### ACKNOWLEDGMENT

The author would again like to thank Dr. R. M. Steinman for providing computer support under AFOSR Grant No. 91-0124.

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