Boundary Conditions for the Pauli Equation: Application to Photodetachment of Cs^-

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We formulate the boundary conditions near the atomic nucleus for solving the Pauli equation, based on the analytic solution of the Dirac equation for a Coulomb potential. We then integrate the Pauli equation using an effective potential that is adjusted to reproduce Dirac R-matrix scattering phase shifts, and find the $^3P_1^o$ resonance contribution to the photodetachment cross section of Cs^-. Our photodetachment cross sections agree with recent experiments by Scheer *et al.* [Phys. Rev. Lett. **80**, 684 (1998)] after tuning the resonance position by 2.4 meV. We also provide angle-differential photodetachment cross sections and the corresponding asymmetry parameter β near the Cs($6s$) threshold.

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Spin-orbit interaction effects in atomic physics are often treated by adding the term

$$V_{LS} = \frac{1}{2m^2c^2}\,\frac{1}{r}\,\frac{dV}{dr}\,\mathbf{s}\cdot\mathbf{l} \tag{1}$$

to the nonrelativistic potential V and solving the Schrödinger equation with a modified potential for a two-component wave function, which is also called the Pauli equation. For a Coulomb potential energy $W = Ve = -Ze^2/r$, Eq. (1) leads to a nonphysical singularity $1/r^3$ near the origin. This singularity does not cause problems if the spin-orbit interaction is treated perturbatively. In this case, the expectation value of the interaction (1) is not divergent for $l > 0$ because the radial wave function behaves as r^l near the origin, and at $l = 0$ it can be shown that the spin-orbit interaction term is identically equal to zero. A more rigorous treatment [1,2], based on the Dirac equation, suggests that the interaction (1) should be regularized by using either the factor $(1 - W/2mc^2)^{-1}$ [1] or $(1 - W/2mc^2)^{-2}$ [2,3]. This ambiguity is connected to the ambiguity in defining a Hermitian energy-independent Hamiltonian for the Pauli equation when going from two first-order Dirac equations for the large and small components of the relativistic wave function to one second-order Schrödinger-Pauli equation. Such a regularization can be done only in the approximation $W \ll mc^2$. However, this condition breaks down at distances $r < e^2Z/mc^2$. This difficulty was addressed in several atomic structure calculations [4] where regular Pauli Hamiltonians were derived and used in self-consistent many-body calculations of bound states. This problem also should be addressed in calculations of Pauli wave functions for continuum states. In the theoretical treatment of photodetachment (PD), the behavior of the final-state wave function at the origin affects the phase and amplitude of the wave function in the intermediate region, which is important for the calculation of PD matrix elements. This becomes particularly critical if we try to describe effects which are forbidden in the LS-coupling approximation.

A good example is PD of Cs^- through the $^3P_1^o$ resonance observed recently by Scheer *et al.* [5]. This was the first direct experimental confirmation of earlier theoretical predictions [6,7] of the $Cs^-(6s6p^3P_J^o)$ resonance state that lies a few meV above the Cs($6s$) threshold. However, theoretical calculations of PD cross sections have not been performed thus far. In the present paper, we formulate boundary conditions for the Pauli equation for the final-state electron wave function, and apply them to the description of PD near the detachment threshold of the Cs^- ion. Our results confirm the existence of a "bump," indicative of a $^3P_1^o$ resonance, on the Wigner p-wave scattering background in the total PD cross section.

Our method starts with separating the entire space into two regions: In the inner region bound by a sphere of radius r_0, the only important nonrelativistic interaction is the unscreened Coulomb interaction between the detaching electron and the nucleus. In this region, relativistic interactions (i.e., the spin-orbit interaction for electrons with low angular momentum and the relativistic mass correction) are important, and the total angular momentum quantum number of the detaching electron, j, is conserved, making the jj representation a natural choice. At $r > r_0$, we will neglect the Coulomb potential energy $-Ze^2/r$ compared to the electron rest energy mc^2. In this region, the effective potential is not diagonal in the jj representation because of the exchange effects, and the LS representation is more appropriate, where L is the total orbital angular momentum and S is the total spin of the atom + electron system. The effective potential is not diagonal in the LS representation due to spin-orbit interaction effects; however, the off-diagonal elements are small. We estimate the radius r_0 for Cs ($Z = 55$) as 0.01 a.u.

In the inner region, for $r < r_0$, we use the well-known analytic solution of the Dirac equation for an electron in the Coulomb potential. At $r = r_0$, we transform the Dirac wave function for $r < r_0$ into the Pauli wave function ψ. The standard transformation for this purpose [8,9] (hereafter we use atomic units)

$$\psi = (1 + \mathbf{p}^2/8c^2)\psi_A\,, \tag{2}$$

where ψ_A is the large component of the Dirac wave function and $\mathbf{p}$ is the momentum operator, neglects V compared to c^2. The transformation (2) gives a Pauli wave function ψ which is only approximately normalized [8]. If we do not neglect V compared to c^2 (but disregard the nonrelativistic part of the total electron energy), Eq. (2) becomes

$$\psi = [1 + \boldsymbol{\sigma}\cdot\mathbf{p}f(r)\boldsymbol{\sigma}\cdot\mathbf{p}]\psi_A\,, \tag{3}$$

where $f(r) = [8c^2(1 - V/2c^2)^2]^{-1}$. By using standard properties of the Pauli matrices $\boldsymbol{\sigma}$, Eq. (3) can be rewritten as

$$\psi = \left(1 - \frac{df}{dr}\frac{d}{dr} - f\nabla^2 - \frac{1}{r}\frac{df}{dr}\boldsymbol{\sigma}\cdot\mathbf{l}\right)\psi_A\,. \tag{4}$$

Finally, after the separation of the spin and angular variables, we obtain the corresponding relation between the p-wave Schrödinger radial function $u(r)$ and the large component of the Dirac radial function $G(r)$,

$$u_j(r) = \left\{1 - r\frac{df}{dr}\frac{d}{dr}\frac{1}{r} - f\left[\frac{d^2}{dr^2} - \frac{2}{r^2}\right] - \frac{1}{r}\frac{df}{dr}\left[j(j+1) - \frac{11}{4}\right]\right\}G_\kappa(r)\,, \tag{5}$$

where κ is the relativistic quantum number of the Dirac theory. For PD from an S state, $j = 1/2$ or $3/2$.

After calculating $u_j(r)$ in the jj representation, we transform it into the LS representation and integrate numerically the system of two coupled equations (for $S = 0$ and $S = 1$) at $r > r_0$. Since we are interested in near-threshold PD for energies much lower than the $6s$-$6p_{1/2}$ excitation energy of the neutral Cs, we have chosen to describe the effective interaction of the electron with the Cs atom by an LS dependent pseudopotential [3] which is adjusted to reproduce the low-energy scattering eigenphases for $J \le 2$ and odd parity obtained from the Dirac R-matrix calculations [7,10]. We describe the P states of Cs^- by

$$V_P(r) = -\frac{Z}{r}e^{-\lambda r} - Ae^{-\gamma r} - \frac{\alpha}{2r^4}[1 - e^{-(r/r_c)^6}] + V_{LS}\,, \tag{6}$$

while the pseudopotential for the S state is

$$V_S(r) = -\frac{A}{r}e^{-\gamma r} - \frac{\alpha}{2r^4}[1 - e^{-(r/r_c)^6}] + V_{LS}\,. \tag{7}$$

The nuclear charge is $Z = 55$, $\alpha = 402.2$ is the atomic polarizability for the ground state of Cs, and $\lambda = 7.2443$ is the nuclear screening parameter. Except for λ, all other fit parameters in Eqs. (6) and (7) depend on L and S and are given in Table I. Since the spin-orbit interaction term vanishes for the $^1S^e$ state, the first term in Eq. (6) has a weak influence. In contrast, for the $^3P^o$ state, we found that position and width of the $Cs^-(^3P^o_J)$ resonances are very sensitive to the near-nuclear region where the interaction (1) is important. As a test case of the nonrelativistic pseudopotentials, we have performed similar calculations for PD of Na^- and found very good agreement with recent many-body R-matrix eigenchannel calculations [11] for energies up to 0.7 eV above the detachment threshold.

TABLE I. The fit parameters A, γ, and r_c for the pseudopotentials $V_S(r)$ in Eq. (7) and $V_P(r)$ in Eq. (6) used to reproduce the scattering phase shifts provided by Dirac R-matrix calculations [10].

State	A	γ	r_c
$^1S^e$	4.5396	1.3304	1.6848
$^1P^o$	−3.6681	1.3195	1.8031
$^3P^o$	4.1271	2.2329	2.1271

For $L = 1$, the matrix elements of the $\mathbf{s}\cdot\mathbf{l}$ operator in LS representation,

$$A^J_{SS'} = \langle LSJM_J|\mathbf{s}\cdot\mathbf{l}|L'S'JM_J\rangle\,, \tag{8}$$

are $A^1_{00} = 0$, $A^1_{11} = -1/2$, $A^1_{01} = 1/\sqrt{2}$. These values are sufficient for solving the PD problem, but, in order to fit all potential parameters, we also need to calculate eigenphases for $J = 0$ and $J = 2$, where (for $L = 1$) $A^0_{11} = -1$, $A^2_{11} = 1/2$. The different values of A^J_{11} are responsible for the splitting of the lowest $^3P^o$ resonance into three J components.

To calculate the PD cross section, we introduce the radial function $u_b(r)$ describing the initial $^1S^e$ bound state, and the final-state radial wave function $u^J_{S'S}$ with the following asymptotic behavior:

$$u^J_{S'S}(r) \sim \sin(kr - L\pi/2)\delta_{S'S} + \exp[-i(kr - L\pi/2)](f^J_{S'S})^*, \tag{9}$$

where $f^J_{S'S}$ is the matrix of scattering amplitudes. Introducing the PD matrix element,

$$M_S = \int [u^1_{0S}(r)]^* r u_b(r)\, dr\,, \tag{10}$$

we obtain the differential PD cross section into a final state with the total spin S,

$$\frac{d\sigma_S}{d\Omega} = \frac{8\pi\omega}{3ck}|M_S|^2 \sum_{M_S M_L} |C^{10}_{1M_L SM_S} Y_{1M_L}(\hat{k})|^2, \tag{11}$$

where ω is the photon frequency, and $\hat{k}$ is the unit vector in the direction of the photodetached electron relative to the unit polarization vector of an incident linearly polarized photon. Note that we use the *length* form for the perturbation operator, which is appropriate for calculations involving pseudopotentials [12].

From Eq. (11), we can see the advantage of using the Pauli wave function instead of the Dirac wave function for the study of near-threshold PD processes: The contribution of different S terms can be identified easily in the PD cross section. PD just above the ground state of the Cs atom is dominated by a p-wave contribution to the final state. By using Eq. (11), the contribution of the $^3P^o$

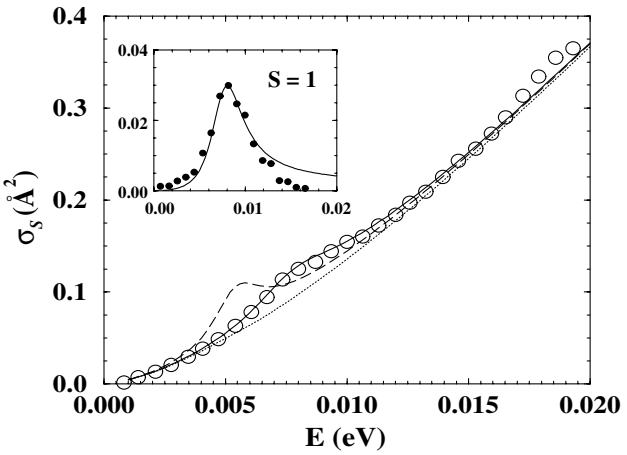

FIG. 1. Angle-integrated PD cross sections of Cs^- near the detachment threshold. Dotted curve: $S = 0$ contribution only; dashed curve: total cross section for the fit parameters in Table I; solid curve: after adjusting the parameter r_c in the final $^3P^o$ state to 2.1294. Circles show the experimental data from Fig. 2 of Ref. [5]. The inset shows our calculated $S = 1$ contribution to the detachment cross section (thick solid curve) compared to the background-subtracted measurement (dots) from Fig. 3 of Ref. [5]. The sizes of the circles and dots indicate the experimental error [5].

resonance can be isolated from that of the $^1P^o$ which gives the background in the PD cross section.

Figure 1 gives the total PD cross section, $\sigma = \sigma_0 + \sigma_1$, for energies of the photoelectron just above the detachment threshold of Cs^-. Our calculations based on the R-matrix Dirac results for eigenphases [10] exhibit a local peak whose position, 5.6 meV above the threshold, is somewhat lower than the observed peak at 8 meV [5], and the theoretical width of 2.7 meV is smaller than the experimental value of 5 meV. Therefore, we have tuned the position of the $J = 1$ resonance by changing the parameter r_c in Eq. (6) for the $^3P^o$ symmetry from 2.1271 to 2.1294. This modification has shifted the position of the $J = 1$ resonance to 8 meV. The resulting curve, also shown in Fig. 1, agrees with the experimental data from Fig. 2 of Ref. [5], with respect to both the resonance position and the width. The inset shows that part of the background under the resonance peak originates in an increasing $S = 1$ contribution for higher energies. By using modified pseudopotentials with $r_c = 2.1294$, the $J = 0$ and $J = 2$ terms of the $^3P^o$ resonance are shifted from 1.7 and 12.7 meV, as found in Dirac R-matrix calculations for electron scattering [10], to 4 and 16 meV, respectively. This gives a Landé constant for the $^3P^o$ state of 4 meV instead of 3.7 meV in [10].

It should be emphasized that the use of the correct boundary conditions at the origin is important for obtaining the correct $S = 1$ contribution to the $^3P^o_1$ resonance (the $S = 0$ contribution gives the PD background, which follows the Wigner threshold law, $E^{3/2}$, for p-wave scattering, cf. Fig. 1). For example, using the $(1 - V/2c^2)^{-2}$ regularization [2,3], while integrating the Pauli equation from the origin, reduces the $S = 1$ contribution by a factor of 1.5, and the $(1 - V/2c^2)^{-1}$ regularization [1] by 14%.

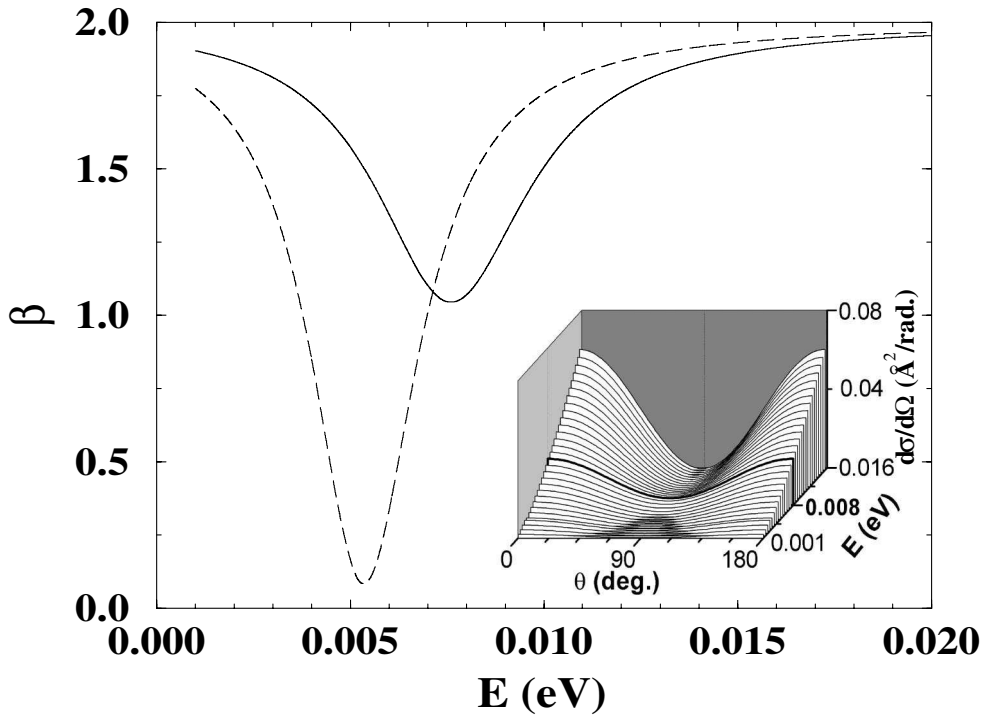

FIG. 2. Asymmetry parameter for the two models corresponding to two cross sections in Fig. 1. The inset shows the corresponding angle-differential photodetachment cross section [cf. Eq. (12)].

In the angular distribution of photoelectrons [Eq. (11)], the $S = 1$ contribution adds a $\sin^2\theta$ term to the pure $\cos^2\theta$ dependence of the $S = 0$ contribution. Therefore, the asymmetry parameter β [β is a measure of the deviation of the photoelectrons distribution from isotropy ($\beta = 0$), and completely characterizes the shape of the emission pattern.] [13] in

$$\frac{d\sigma}{d\Omega} = \frac{\sigma[1 + \beta P_2(\cos\theta)]}{4\pi} \tag{12}$$

differs from its maximum value 2. In Eq. (12), both the angle-integrated, σ, and the angle-differential, $d\sigma/d\Omega$, PD cross sections include the summation over the final spin $S = 0$ and 1 states. $P_2(\cos\theta)$ is the Legendre polynomial for $l = 2$, and θ is the polar angle of the unit vector $\hat{k}$ in Eq. (11). Figure 2 shows the energy dependence of β for the two calculations described above and (as inset) the corresponding angle-differential cross section. This theoretical prediction may be useful for future experimental attempts to detect the $^3P^o$ resonance in Cs^-.

In conclusion, we have formulated boundary conditions for solving the Pauli equation, which are important for the description of the spin-orbit interaction effects in electron scattering and PD processes. The application of this method to the near-threshold PD of Cs^- allows us to calculate the contribution of the $^3P_1^o$ resonance in very good agreement with the experimental results in [5].

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