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Notes

Ingoing and outgoing waves in the non-relativistic theory of photoionization

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Abstract

A well-known formula for the differential cross section for photoionization contains a so-called 'final state' wave function which asymptotically behaves as a Coulomb-modified plane wave plus an *ingoing* Coulomb-modified radial wave. We explain the reason of appearance of that function on the ground of an analysis of an asymptotic form of a relevant *outgoing* Green's function. The reasoning is carried out without referring to an intuitive argumentation of Breit and Bethe [Phys. Rev. 93 (1954) 888].

Keywords: Photoionization cross-section; Final-state wave function; Schrödinger equation; Coulomb Green's function

1. Introduction

Using the Golden Rule, it may be shown [1–5] that a differential cross section for one-photon ionization of a non-relativistic one-electron system by a plane electromagnetic wave of wave vector $\boldsymbol{\kappa}$, frequency $\omega = \kappa c$, and polarization $\boldsymbol{\varepsilon}$ is given by

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\hbar k \alpha}{2\pi m \omega} |\langle \psi_{\mathrm{f}}^{(0)} | \mathrm{e}^{\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \boldsymbol{\nabla} \psi_{\mathrm{i}}^{(0)} \rangle|^2. \tag{1.1}$$

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Here k is the wave number of the ejected photoelectron, $\alpha = e^2/4\pi\varepsilon_0 c\hbar$ is Sommerfeld's fine structure constant, while m and e stand for electron's mass and an absolute value of its charge, respectively. The functions $\psi_{\mathrm{i}}^{(0)}(\boldsymbol{r})$ and $\psi_{\mathrm{f}}^{(0)}(\boldsymbol{r})$ are solutions to the time-independent Schrödinger equation in the absence of the electromagnetic wave. The former one, $\psi_{\mathrm{i}}^{(0)}(\boldsymbol{r})$, describes an initial stationary bound state of the electron; it decays exponentially for $r \to \infty$. The latter one, $\psi_{\mathrm{f}}^{(0)}(\boldsymbol{r})$, is usually said to describe a final continuum state of the photoelectron propagating toward a detector.

A shortcoming of the Golden Rule is that it does not determine the 'final state' wave function $\psi_{\mathrm{f}}^{(0)}(\boldsymbol{r})$ uniquely, leaving open the question concerning its asymptotic form. To fill in this gap, one usually refers [1,3,4,6–8] to an intuitive reasoning presented half a century ago by Breit and Bethe [9]. It is the purpose of this paper to present an alternative (i.e., without referring to the Golden Rule) derivation of formula (1.1), from which the asymptotic form of $\psi_{\mathrm{f}}^{(0)}(\boldsymbol{r})$ results in the natural manner with no need to invoke the arguments of Breit and Bethe.

2. Outflow of photoelectrons

Consider a non-relativistic electron which initially, for $t < t_0$, has been in a bound stationary state

$$\Psi^{(0)}(\boldsymbol{r}, t) = \psi_{\mathrm{i}}^{(0)}(\boldsymbol{r})\mathrm{e}^{-\mathrm{i}\omega^{(0)}t} \tag{2.1}$$

(with $E^{(0)} = \hbar\omega^{(0)}$ below the ionization threshold set at zero energy), obeying

$$\left[\hat{\mathscr{H}}^{(0)}(\boldsymbol{r}) - \mathrm{i}\hbar\frac{\partial}{\partial t}\right]\Psi^{(0)}(\boldsymbol{r}, t) = 0, \tag{2.2}$$

where

$$\hat{\mathscr{H}}^{(0)}(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r} + V(\boldsymbol{r}) \tag{2.3}$$

with $Z \geqslant 0$ and $V(\boldsymbol{r})$ denoting a real potential, in general non-central, which asymptotically falls-off faster than r^{-2}. Let for $t > t_0$ the electron is driven by the classical electromagnetic field of the form of a polarized plane wave characterized, in the Coulomb gauge, by the vector potential

$$\boldsymbol{A}(\boldsymbol{r}, t) = A\boldsymbol{\varepsilon}\cos(\boldsymbol{\kappa}\cdot\boldsymbol{r} - \omega t). \tag{2.4}$$

We shall assume that

$$E_- = \hbar\omega_- = \hbar(\omega^{(0)} - \omega) \tag{2.5}$$

is not in the spectrum of the Hamiltonian $\hat{\mathscr{H}}^{(0)}(\boldsymbol{r})$ and that

$$E_+ = \hbar\omega_+ = \hbar(\omega^{(0)} + \omega) > 0, \tag{2.6}$$

i.e., the driving electromagnetic field may ionize the electron. The time-dependent Schrödinger equation describing electron's dynamics in the field is

$$\left[\hat{\mathscr{H}}^{(0)}(\boldsymbol{r}) + \hat{\mathscr{H}}^{(1)}(\boldsymbol{r}, t) + \hat{\mathscr{H}}^{(2)}(\boldsymbol{r}, t) - \mathrm{i}\hbar\frac{\partial}{\partial t}\right]\Psi(\boldsymbol{r}, t) = 0 \tag{2.7}$$

with $\hat{\mathscr{H}}^{(0)}(\boldsymbol{r})$ defined in Eq. (2.3),

$$\hat{\mathscr{H}}^{(1)}(\boldsymbol{r}, t) = -\frac{\mathrm{i}e\hbar}{m}\boldsymbol{A}(\boldsymbol{r}, t) \cdot \boldsymbol{\nabla}, \tag{2.8}$$

and

$$\hat{\mathscr{H}}^{(2)}(\boldsymbol{r}, t) = \frac{e^2}{2m}\boldsymbol{A}^2(\boldsymbol{r}, t). \tag{2.9}$$

Assuming that the driving electromagnetic field perturbs weakly the initial electronic state, for times when switching effects may be already neglected but the photoionization probability is still small, we shall seek solutions to Eq. (2.7) in the form of the perturbation series

$$\Psi(\boldsymbol{r}, t) = \Psi^{(0)}(\boldsymbol{r}, t) + \Psi^{(1)}(\boldsymbol{r}, t) + \Psi^{(2)}(\boldsymbol{r}, t) + \cdots. \tag{2.10}$$

On substituting series (2.10) into Eq. (2.7), after equating terms of the same order in the perturbation, we infer the following equations:

$$\left[\hat{\mathscr{H}}^{(0)}(\boldsymbol{r}) - \mathrm{i}\hbar\frac{\partial}{\partial t}\right]\Psi^{(1)}(\boldsymbol{r}, t) = -\hat{\mathscr{H}}^{(1)}(\boldsymbol{r}, t)\Psi^{(0)}(\boldsymbol{r}, t), \tag{2.11}$$

$$\left[\hat{\mathscr{H}}^{(0)}(\boldsymbol{r}) - \mathrm{i}\hbar\frac{\partial}{\partial t}\right]\Psi^{(2)}(\boldsymbol{r}, t) = -\hat{\mathscr{H}}^{(1)}(\boldsymbol{r}, t)\Psi^{(1)}(\boldsymbol{r}, t) - \hat{\mathscr{H}}^{(2)}(\boldsymbol{r}, t)\Psi^{(0)}(\boldsymbol{r}, t) \tag{2.12}$$

obeyed by the first- and second-order corrections to $\Psi^{(0)}(\boldsymbol{r}, t)$.

In the perturbed state $\Psi(\boldsymbol{r}, t)$ the electron's probability current density is

$$\boldsymbol{j}(\boldsymbol{r}, t) = \frac{\hbar}{m}\mathrm{Im}\,[\Psi^*(\boldsymbol{r}, t)\boldsymbol{\nabla}\Psi(\boldsymbol{r}, t)] + \frac{e}{m}\boldsymbol{A}(\boldsymbol{r}, t)\Psi^*(\boldsymbol{r}, t)\Psi(\boldsymbol{r}, t). \tag{2.13}$$

On substituting here expansion (2.10), we obtain the following perturbation series representation of $\boldsymbol{j}(\boldsymbol{r}, t)$:

$$\boldsymbol{j}(\boldsymbol{r}, t) = \boldsymbol{j}^{(0)}(\boldsymbol{r}, t) + \boldsymbol{j}^{(1)}(\boldsymbol{r}, t) + \boldsymbol{j}^{(2)}(\boldsymbol{r}, t) + \cdots, \tag{2.14}$$

where

$$\boldsymbol{j}^{(0)}(\boldsymbol{r}, t) = \frac{\hbar}{m}\mathrm{Im}\,[\Psi^{(0)*}(\boldsymbol{r}, t)\boldsymbol{\nabla}\Psi^{(0)}(\boldsymbol{r}, t)] \tag{2.15}$$

is the probability current density in the unperturbed state $\Psi^{(0)}(\boldsymbol{r}, t)$, while the first- and second-order corrections, due to the electromagnetic perturbation, are given explicitly by

$$\begin{aligned}\boldsymbol{j}^{(1)}(\boldsymbol{r}, t) = {} & \frac{\hbar}{m}\mathrm{Im}\,[\Psi^{(0)*}(\boldsymbol{r}, t)\boldsymbol{\nabla}\Psi^{(1)}(\boldsymbol{r}, t) + \Psi^{(1)*}(\boldsymbol{r}, t)\boldsymbol{\nabla}\Psi^{(0)}(\boldsymbol{r}, t)] \\ & + \frac{e}{m}\boldsymbol{A}(\boldsymbol{r}, t)\Psi^{(0)*}(\boldsymbol{r}, t)\Psi^{(0)}(\boldsymbol{r}, t)\end{aligned} \tag{2.16}$$

and

$$\begin{aligned}\boldsymbol{j}^{(2)}(\boldsymbol{r}, t) = {} & \frac{\hbar}{m}\mathrm{Im}\,[\Psi^{(0)*}(\boldsymbol{r}, t)\boldsymbol{\nabla}\Psi^{(2)}(\boldsymbol{r}, t) + \Psi^{(1)*}(\boldsymbol{r}, t)\boldsymbol{\nabla}\Psi^{(1)}(\boldsymbol{r}, t) \\ & + \Psi^{(2)*}(\boldsymbol{r}, t)\boldsymbol{\nabla}\Psi^{(0)}(\boldsymbol{r}, t)] + 2\frac{e}{m}\boldsymbol{A}(\boldsymbol{r}, t)\mathrm{Re}\,[\Psi^{(0)*}(\boldsymbol{r}, t)\Psi^{(1)}(\boldsymbol{r}, t)],\end{aligned} \tag{2.17}$$

respectively. Since for $r \to \infty$ the bound state wave function $\Psi^{(0)}(\boldsymbol{r}, t)$ decays exponentially, from Eqs. (2.15) and (2.16) we see that in the asymptotic region $\boldsymbol{j}^{(0)}(\boldsymbol{r}, t)$ and $\boldsymbol{j}^{(1)}(\boldsymbol{r}, t)$ vanish, while on the right-hand side of Eq. (2.17) only the second term in the first square bracket gives the non-vanishing contribution. Consequently, in the asymptotic region, to the second order in the perturbation, we have

$$\boldsymbol{j}(\boldsymbol{r}, t) \overset{r\to\infty}{\longrightarrow} \frac{\hbar}{m} \operatorname{Im}[\Psi^{(1)*}(\boldsymbol{r}, t) \boldsymbol{\nabla} \Psi^{(1)}(\boldsymbol{r}, t)]. \tag{2.18}$$

This implies that henceforth we should focus our interest on the asymptotic form of the first-order wave function correction $\Psi^{(1)}(\boldsymbol{r}, t)$.

We shall seek $\Psi^{(1)}(\boldsymbol{r}, t)$ in the form

$$\Psi^{(1)}(\boldsymbol{r}, t) = \psi_{+}^{(1)}(\boldsymbol{r}) \mathrm{e}^{-\mathrm{i}\omega_{+} t} + \psi_{-}^{(1)}(\boldsymbol{r}) \mathrm{e}^{-\mathrm{i}\omega_{-} t}. \tag{2.19}$$

Plugging Eq. (2.19) into Eq. (2.11), with the aid of Eqs. (2.8), (2.4), and (2.1) we infer the following inhomogeneous equations obeyed by $\psi_{\pm}^{(1)}(\boldsymbol{r})$:

$$[\hat{\mathscr{H}}^{(0)}(\boldsymbol{r}) - E_{\pm}] \psi_{\pm}^{(1)}(\boldsymbol{r}) = -\hat{\mathscr{H}}_{\pm}^{(1)}(\boldsymbol{r}) \psi_{\mathrm{i}}^{(0)}(\boldsymbol{r}), \tag{2.20}$$

where

$$\hat{\mathscr{H}}_{\pm}^{(1)}(\boldsymbol{r}) = -\frac{\mathrm{i}e\hbar A}{2m} \mathrm{e}^{\pm \mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{r}} \boldsymbol{\varepsilon} \cdot \boldsymbol{\nabla}. \tag{2.21}$$

Eqs. (2.20) are to be augmented with appropriate boundary conditions. Since E_{-} is *below* the ionization threshold, $r\psi_{-}^{(1)}(\boldsymbol{r})$ has to vanish at spatial infinity. Consequently, the boundary conditions for $\psi_{-}^{(1)}(\boldsymbol{r})$ are

$$r\psi_{-}^{(1)}(\boldsymbol{r}) \overset{r\to 0}{\longrightarrow} 0, \quad r\psi_{-}^{(1)}(\boldsymbol{r}) \overset{r\to\infty}{\longrightarrow} 0. \tag{2.22}$$

Further, since, by assumption, E_{+} (henceforth denoted as E) is *above* the ionization threshold, $\psi_{+}^{(1)}(\boldsymbol{r}) \exp(-\mathrm{i}\omega_{+} t)$ is just that component of $\Psi^{(1)}(\boldsymbol{r}, t)$ which asymptotically describes the outgoing photoelectrons. Hence, at spatial infinity $\psi_{+}^{(1)}(\boldsymbol{r})$ has to obey the Sommerfeld's radiation condition. Consequently, the boundary conditions for that function are

$$r\psi_{+}^{(1)}(\boldsymbol{r}) \overset{r\to 0}{\longrightarrow} 0, \quad \left(\frac{\partial}{\partial r} - \mathrm{i}k\right) r\psi_{+}^{(1)}(\boldsymbol{r}) \overset{r\to\infty}{\longrightarrow} 0, \tag{2.23}$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}}. \tag{2.24}$$

From the above discussion, we infer that Eq. (2.18) may be rewritten as

$$\boldsymbol{j}(\boldsymbol{r},t) \overset{r\to\infty}{\longrightarrow} \frac{\hbar}{m} \mathrm{Im}\,[\psi_{+}^{(1)*}(\boldsymbol{r})\boldsymbol{\nabla}\psi_{+}^{(1)}(\boldsymbol{r})]. \tag{2.25}$$

It is worth noticing that the right-hand side of this equation is time-independent.

The boundary value problem for $\psi_{+}^{(1)}(\boldsymbol{r})$, constituted by Eqs. (2.20) and (2.23), may be solved with the aid of the Green's functions technique. The solution is

$$\psi_{+}^{(1)}(\boldsymbol{r}) = -\int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \mathscr{G}_{+}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}')\hat{\mathscr{H}}_{+}^{(1)}(\boldsymbol{r}')\psi_{\mathrm{i}}^{(0)}(\boldsymbol{r}'), \tag{2.26}$$

where $\mathscr{G}_{+}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}')$ is the *outgoing* Green's function defined as a solution to the boundary value problem ($\boldsymbol{r}'$ fixed):

$$[\hat{\mathscr{H}}^{(0)}(\boldsymbol{r}) - E]\mathscr{G}_{+}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}'), \tag{2.27}$$

$$r\mathscr{G}_{+}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') \overset{r\to 0}{\longrightarrow} 0, \quad \left(\frac{\partial}{\partial r} - \mathrm{i}k\right) r\mathscr{G}_{+}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') \overset{r\to\infty}{\longrightarrow} 0. \tag{2.28}$$

Some relevant properties of $\mathscr{G}_{+}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}')$, and its ingoing counterpart $\mathscr{G}_{-}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}')$, are derived and discussed briefly in the appendix. In particular, there we show (cf. Eq. (A.25)) that asymptotically it holds ($\boldsymbol{r}'$ fixed)

$$\mathscr{G}_{+}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') \overset{r\to\infty}{\longrightarrow} \frac{m}{2\pi\hbar^2} \frac{\mathrm{e}^{\mathrm{i}kr+\mathrm{i}\eta\ln 2kr}}{r} \psi_{-}^{(0)*}(E,\boldsymbol{n}_r,\boldsymbol{r}'), \tag{2.29}$$

where $\boldsymbol{n}_r = \boldsymbol{r}/r$,

$$\eta = \frac{Z}{ka} \tag{2.30}$$

(with $a = 4\pi\varepsilon_0\hbar^2/me^2$ denoting the Bohr radius), while $\psi_{-}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}')$ is a solution to the time-independent homogeneous Schrödinger equation (cf. Eq. (A.33))

$$[\hat{\mathscr{H}}^{(0)}(\boldsymbol{r}') - E]\psi_{-}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}') = 0 \tag{2.31}$$

and asymptotically is a superposition of a Coulomb-modified plane wave with the wave vector $k\boldsymbol{n}_r$ and a Coulomb-modified radially *ingoing* wave (cf. Eq. (A.34)):

$$\psi_{-}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}') \overset{r'\to\infty}{\longrightarrow} \mathrm{e}^{\mathrm{i}kr'\boldsymbol{n}_r\cdot\boldsymbol{n}'_r+\mathrm{i}\eta\ln[kr'(1+\boldsymbol{n}_r\cdot\boldsymbol{n}'_r)]} + \mathscr{A}_{-}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{n}'_r)\frac{\mathrm{e}^{-\mathrm{i}kr'-\mathrm{i}\eta\ln 2kr'}}{r'} \tag{2.32}$$

with $\boldsymbol{n}_r \nparallel -\boldsymbol{n}'_r$ and with the amplitude $\mathscr{A}_{-}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{n}'_r)$ defined by Eq. (A.35).

Making use of Eq. (2.29) in Eq. (2.26), we arrive at the following asymptotic form of $\psi_{+}^{(1)}(\boldsymbol{r})$:

$$\psi_{+}^{(1)}(\boldsymbol{r}) \overset{r\to\infty}{\longrightarrow} \mathscr{A}_{+}^{(1)}(E,\boldsymbol{n}_r)\frac{\mathrm{e}^{\mathrm{i}kr+\mathrm{i}\eta\ln 2kr}}{r}, \tag{2.33}$$

where

$$\mathscr{A}_{+}^{(1)}(E,\boldsymbol{n}_r) = -\frac{m}{2\pi\hbar^2}\int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}'\, \psi_{-}^{(0)*}(E,\boldsymbol{n}_r,\boldsymbol{r}')\hat{\mathscr{H}}_{+}^{(1)}(\boldsymbol{r}')\psi_{\mathrm{i}}^{(0)}(\boldsymbol{r}'). \tag{2.34}$$

Evidently, Eq. (2.33) is consistent with the radiation condition in Eq. (2.23).

3. Differential cross section

We are now prepared to find the differential cross section characterizing an angular distribution of photoelectrons. It is defined as

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \lim_{r\to\infty}\frac{r^2\boldsymbol{n}_r\cdot\boldsymbol{j}(\boldsymbol{r})}{I} \tag{3.1}$$

(we have suppressed the time dependence of the current density in virtue of the remark following Eq. (2.25)), where

$$I = \frac{\varepsilon_0\omega c A^2}{2\hbar} \tag{3.2}$$

is the photon flux in the driving electromagnetic wave (2.4). In virtue of Eqs. (2.25) and (2.33), the numerator in Eq. (3.1) is

$$\lim_{r\to\infty} r^2\boldsymbol{n}_r\cdot\boldsymbol{j}(\boldsymbol{r}) = \frac{\hbar k}{m}|\mathscr{A}_{+}^{(1)}(E,\boldsymbol{n}_r)|^2, \tag{3.3}$$

which, in conjunction with Eq. (2.34), yields the final result

$$\frac{\mathrm{d}\sigma(E,\boldsymbol{n}_r)}{\mathrm{d}\Omega} = \frac{\hbar k\alpha}{2\pi m\omega}\left|\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}'\,\psi_{-}^{(0)*}(E,\boldsymbol{n}_r,\boldsymbol{r}')\mathrm{e}^{\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{r}'}\boldsymbol{\varepsilon}\cdot\boldsymbol{\nabla}'\psi_{\mathrm{i}}^{(0)}(\boldsymbol{r}')\right|^2. \tag{3.4}$$

Apart from unimportant notational differences, Eq. (3.4) is identical with Eq. (1.1).

Appendix. Asymptotic forms of Green's functions

Let $\hat{H}^{(0)}(\boldsymbol{r})$ denote the Schrödinger–Coulomb Hamiltonian

$$\hat{H}^{(0)}(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r}. \tag{A.1}$$

For $E>0$, we define the outgoing (the upper signs and subscripts) and ingoing (the lower signs and subscripts) Schrödinger–Coulomb Green's functions as solutions to the following inhomogeneous boundary-value problems ($\boldsymbol{r}'$ fixed):

$$[\hat{H}^{(0)}(\boldsymbol{r}) - E]G_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}'), \tag{A.2}$$

$$rG_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') \xrightarrow{r\to 0} 0, \quad \left(\frac{\partial}{\partial r}\mp \mathrm{i}k\right)rG_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') \xrightarrow{r\to\infty} 0 \tag{A.3}$$

with k defined in Eq. (2.24). The spherical partial-wave expansions of $G_{\pm}^{(0)}(E, \boldsymbol{r}, \boldsymbol{r}')$ are

$$G_{\pm}^{(0)}(E, \boldsymbol{r}, \boldsymbol{r}') = \sum_{l=0}^{\infty} \sum_{m_l=-l}^{l} \frac{g_{l\pm}^{(0)}(E, r, r')}{rr'} Y_{lm_l}(\boldsymbol{n}_r) Y_{lm_l}^{*}(\boldsymbol{n}_r'), \tag{A.4}$$

where $Y_{lm_l}(\boldsymbol{n}_r)$, with $\boldsymbol{n}_r = \boldsymbol{r}/r$, are normalized spherical harmonics and

$$g_{l\pm}^{(0)}(E, r, r') = \frac{2m}{\hbar^2 k} F_l(-\eta, kr_<) E_{l\pm}(-\eta, kr_>) \tag{A.5}$$

are radial Green functions with η defined in Eq. (2.30), $r_< = \min(r, r')$, $r_> = \max(r, r')$, and

$$E_{l\pm}(-\eta, \rho) = G_l(-\eta, \rho) \pm \mathrm{i} F_l(-\eta, \rho). \tag{A.6}$$

In Eq. (A.6), $F_l(-\eta, \rho)$ and $G_l(-\eta, \rho)$ are the regular and irregular Coulomb wave functions [10], respectively, with asymptotic forms

$$F_l(-\eta, \rho) \overset{\rho \to \infty}{\longrightarrow} \sin\left[\rho + \eta \ln 2\rho - \frac{\pi l}{2} - \sigma_l(\eta)\right], \tag{A.7}$$

$$G_l(-\eta, \rho) \overset{\rho \to \infty}{\longrightarrow} \cos\left[\rho + \eta \ln 2\rho - \frac{\pi l}{2} - \sigma_l(\eta)\right], \tag{A.8}$$

while

$$\sigma_l(\eta) = \arg \Gamma(l + 1 + \mathrm{i}\eta) = -\sigma_l(-\eta) \quad (\eta \in \mathbb{R}) \tag{A.9}$$

is the Coulomb phase shift. Since

$$r \to \infty \quad \Rightarrow \quad r_> = r, \quad r_< = r' \tag{A.10}$$

and

$$E_{l\pm}(-\eta, \rho) \overset{\rho \to \infty}{\longrightarrow} \exp\left\{\pm \mathrm{i}\left[\rho + \eta \ \ln \ 2\rho - \frac{\pi l}{2} - \sigma_l(\eta)\right]\right\}, \tag{A.11}$$

asymptotically we find

$$G_{\pm}^{(0)}(E, \boldsymbol{r}, \boldsymbol{r}') \overset{r \to \infty}{\longrightarrow} \frac{m}{2\pi\hbar^2} \frac{\mathrm{e}^{\pm \mathrm{i}kr \pm \mathrm{i}\eta \ln 2kr}}{r} \phi_{\mp}^{(0)*}(E, \boldsymbol{n}_r, \boldsymbol{r}'), \tag{A.12}$$

where

$$\phi_{\mp}^{(0)}(E, \boldsymbol{n}_r, \boldsymbol{r}') = \sum_{lm_l} 4\pi \mathrm{i}^l \mathrm{e}^{\mp \mathrm{i}\sigma_l(-\eta)} \frac{F_l(-\eta, kr')}{kr'} Y_{lm_l}(\boldsymbol{n}_r') Y_{lm_l}^{*}(\boldsymbol{n}_r). \tag{A.13}$$

It follows from Eq. (A.13) that $\phi_{\mp}^{(0)}(E, \boldsymbol{n}_r, \boldsymbol{r}')$ are related through

$$\phi_{-}^{(0)}(E, \boldsymbol{n}_r, \boldsymbol{r}') = \phi_{+}^{(0)*}(E, -\boldsymbol{n}_r, \boldsymbol{r}'). \tag{A.14}$$

Clearly, the functions $\phi_{\mp}^{(0)}(E, \boldsymbol{n}_r, \boldsymbol{r}')$ are solutions to the Schrödinger–Coulomb equation

$$[\hat{H}^{(0)}(\boldsymbol{r}') - E]\phi_{\mp}^{(0)}(E, \boldsymbol{n}_r, \boldsymbol{r}') = 0. \tag{A.15}$$

It was shown by Gordon [11] that the asymptotic form of $\phi_{+}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}')$ is

$$\phi_{+}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}') \overset{r'\to\infty}{\longrightarrow} \mathrm{e}^{\mathrm{i}kr'\boldsymbol{n}_r\cdot\boldsymbol{n}'_r-\mathrm{i}\eta\ln[kr'(1-\boldsymbol{n}_r\cdot\boldsymbol{n}'_r)]} + A_{+}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{n}'_r)\frac{\mathrm{e}^{\mathrm{i}kr'+\mathrm{i}\eta\ln 2kr'}}{r'} \quad (\boldsymbol{n}_r \nparallel \boldsymbol{n}'_r), \tag{A.16}$$

where

$$A_{+}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{n}'_r) = \frac{\eta}{k}\frac{\mathrm{e}^{\mathrm{i}\eta\ln[(1-\boldsymbol{n}_r\cdot\boldsymbol{n}'_r)/2]-2\mathrm{i}\sigma_0(\eta)}}{1-\boldsymbol{n}_r\cdot\boldsymbol{n}'_r} \tag{A.17}$$

is the Coulomb scattering amplitude. From this and from Eq. (A.14) we infer that

$$\phi_{-}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}') \overset{r'\to\infty}{\longrightarrow} \mathrm{e}^{\mathrm{i}kr'\boldsymbol{n}_r\cdot\boldsymbol{n}'_r+\mathrm{i}\eta\ln[kr'(1+\boldsymbol{n}_r\cdot\boldsymbol{n}'_r)]} + A_{-}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{n}'_r)\frac{\mathrm{e}^{-\mathrm{i}kr'-\mathrm{i}\eta\ln 2kr'}}{r'} \quad (\boldsymbol{n}_r \nparallel -\boldsymbol{n}'_r), \tag{A.18}$$

where

$$A_{-}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{n}'_r) = A_{+}^{(0)*}(E,-\boldsymbol{n}_r,\boldsymbol{n}'_r) = \frac{\eta}{k}\frac{\mathrm{e}^{-\mathrm{i}\eta\ln[(1+\boldsymbol{n}_r\cdot\boldsymbol{n}'_r)/2]+2\mathrm{i}\sigma_0(\eta)}}{1+\boldsymbol{n}_r\cdot\boldsymbol{n}'_r}. \tag{A.19}$$

Let

$$\hat{\mathscr{H}}^{(0)}(\boldsymbol{r}) = \hat{H}^{(0)}(\boldsymbol{r}) + V(\boldsymbol{r}), \tag{A.20}$$

where $V(\boldsymbol{r})$ is a local sufficiently regular real potential which vanishes asymptotically faster than r^{-2}. If $E>0$, the outgoing (the upper signs and subscripts) and ingoing (the lower signs and subscripts) Green's functions associated with the Hamiltonian $\hat{\mathscr{H}}^{(0)}(\boldsymbol{r})$ are defined as solutions to the boundary-value problems ($\boldsymbol{r}'$ fixed):

$$[\hat{\mathscr{H}}^{(0)}(\boldsymbol{r}) - E]\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}'), \tag{A.21}$$

$$r\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') \overset{r\to 0}{\longrightarrow} 0, \quad \left(\frac{\partial}{\partial r} \mp \mathrm{i}k\right) r\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') \overset{r\to\infty}{\longrightarrow} 0. \tag{A.22}$$

Upon rewriting Eq. (A.21) in the form

$$[\hat{H}^{(0)}(\boldsymbol{r}) - E]\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}') - V(\boldsymbol{r})\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') \tag{A.23}$$

and making use of the Schrödinger–Coulomb Green's functions $G_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}')$, one derives the following integral equations:

$$\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') = G_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') - \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}''\, G_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}'')V(\boldsymbol{r}'')\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r}'',\boldsymbol{r}') \tag{A.24}$$

obeyed by $\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}')$. From Eq. (A.24) and from the asymptotic forms (A.12) of $G_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}'')$ one infers that

$$\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') \overset{r\to\infty}{\longrightarrow} \frac{m}{2\pi\hbar^2}\frac{\mathrm{e}^{\pm\mathrm{i}kr\pm\mathrm{i}\eta\ln 2kr}}{r}\psi_{\mp}^{(0)*}(E,\boldsymbol{n}_r,\boldsymbol{r}'), \tag{A.25}$$

where

$$\psi_{\mp}^{(0)*}(E,\boldsymbol{n}_r,\boldsymbol{r}') = \phi_{\mp}^{(0)*}(E,\boldsymbol{n}_r,\boldsymbol{r}') - \int_{\mathbb{R}^3} \mathrm{d}^3\boldsymbol{r}''\, \phi_{\mp}^{(0)*}(E,\boldsymbol{n}_r,\boldsymbol{r}'')V(\boldsymbol{r}'')\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r}'',\boldsymbol{r}'). \tag{A.26}$$

To say more about the functions $\psi_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}')$, we rewrite Eq. (A.2) in the form

$$[\hat{\mathscr{H}}^{(0)}(\boldsymbol{r})-E]G_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}')=\delta(\boldsymbol{r}-\boldsymbol{r}')+V(\boldsymbol{r})G_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}') \tag{A.27}$$

and employ the Green's functions $\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}')$. This yields the integral equations

$$G_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}')=\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}')+\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}''\,\mathscr{G}_{\pm}^{(0)}(E,\boldsymbol{r},\boldsymbol{r}'')V(\boldsymbol{r}'')G_{\pm}^{(0)}(E,\boldsymbol{r}'',\boldsymbol{r}'). \tag{A.28}$$

After utilizing the asymptotic representations (A.12) and (A.25), we arrive at the following integral equation for $\psi_{\mp}^{(0)*}(E,\boldsymbol{n}_r,\boldsymbol{r}')$:

$$\phi_{\mp}^{(0)*}(E,\boldsymbol{n}_r,\boldsymbol{r}')=\psi_{\mp}^{(0)*}(E,\boldsymbol{n}_r,\boldsymbol{r}')+\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}''\,\psi_{\mp}^{(0)*}(E,\boldsymbol{n}_r,\boldsymbol{r}'')V(\boldsymbol{r}'')G_{\pm}^{(0)}(E,\boldsymbol{r}'',\boldsymbol{r}'). \tag{A.29}$$

Performing then the complex conjugation and applying the reciprocity relation

$$G_{+}^{(0)*}(E,\boldsymbol{r},\boldsymbol{r}')=G_{-}^{(0)}(E,\boldsymbol{r}',\boldsymbol{r}), \tag{A.30}$$

following from Eqs. (A.4)–(A.6), we transform Eq. (A.29) into

$$\psi_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}')=\phi_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}')-\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}''\,G_{\mp}^{(0)}(E,\boldsymbol{r}',\boldsymbol{r}'')V(\boldsymbol{r}'')\psi_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}''). \tag{A.31}$$

Now, acting on this equation from the left with the operator $\left[\hat{H}^{(0)}(\boldsymbol{r}')-E\right]$ and utilizing Eq. (A.2) yields

$$[\hat{H}^{(0)}(\boldsymbol{r}')-E]\psi_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}')=-V(\boldsymbol{r}')\psi_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}') \tag{A.32}$$

and this implies that the functions $\psi_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}')$ are solutions to the Schrödinger equation

$$[\hat{\mathscr{H}}^{(0)}(\boldsymbol{r}')-E]\psi_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}')=0. \tag{A.33}$$

From Eqs. (A.31), (A.12), (A.16), and (A.18) it follows that $\psi_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}')$ have the following asymptotic forms:

$$\psi_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}')\overset{r'\to\infty}{\longrightarrow}\mathrm{e}^{\mathrm{i}kr'\boldsymbol{n}_r\cdot\boldsymbol{n}'_r\pm\mathrm{i}\eta\ln[kr'(1\pm\boldsymbol{n}_r\cdot\boldsymbol{n}'_r)]}+\mathscr{A}_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{n}'_r)\frac{\mathrm{e}^{\mp\mathrm{i}kr'\mp\mathrm{i}\eta\ln 2kr'}}{r'}\,(\boldsymbol{n}_r\nparallel\mp\boldsymbol{n}'_r), \tag{A.34}$$

where

$$\mathscr{A}_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{n}'_r)=A_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{n}'_r)\\ -\frac{m}{2\pi\hbar^2}\int_{\mathbb{R}^3}\mathrm{d}^3\boldsymbol{r}''\,\phi_{\mp}^{(0)*}(E,\boldsymbol{n}'_r,\boldsymbol{r}'')V(\boldsymbol{r}'')\psi_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{r}''), \tag{A.35}$$

with $A_{\mp}^{(0)}(E,\boldsymbol{n}_r,\boldsymbol{n}'_r)$ given by Eqs. (A.17) and (A.19).

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