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Elastic Photon Scattering Cross Section for the H^- Ion in the Asymptotic Approximation

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A comparison is made between the calculation of the elastic photon scattering differential cross section for the H^- ion in the asymptotic approximation, employing both the dipole length and dipole velocity formulations. The divergence of the cross section using the dipole velocity formulation is discussed.

On fait une comparaison du calcul de la section efficace différentielle élastique de diffusion des photons par l'ion H^- dans l'approximation asymptotique en employant les formulations en terme de longueur dipolaire et de vitesse dipolaire. La divergence dans la section efficace par l'emploi de la vitesse dipolaire est discutée.

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Introduction

There has been renewed interest in the H^- ion, particularly with regard to the application of the asymptotic approximation. Adelman (1972, 1973) has recently calculated the static and dynamic polarizabilities of the H^- ion, for which he found fairly close agreement with the results of extended basis set calculations. A problem which has received wide attention, is the discrepancy between calculations of transition matrix elements within the dipole length and dipole velocity formulations, when approximate eigenstates are employed (Crossley 1969). For extended basis set calculations, the dipole velocity results for H^- appear to be in better agreement with experiment (Branscomb 1962).

In this paper, we show within the framework of the asymptotic approximation, that the dipole velocity formulation leads to a differential elastic photon scattering cross section which is divergent. This contrasts with the situation for the dipole length formulation, for which finite results are obtained. The difference between these formalisms and a clear exposition of the mathematical origin of the divergence is shown. This is carried out by converting the appropriate sum over intermediate states to the corresponding differential equation. For the H^- ion, this differential equation is soluble in the asymptotic approximation, for both the dipole length and the dipole velocity formulations.

Theory

The differential elastic photon scattering cross section in the dipole velocity formulation is given by

$$[1] \quad d\sigma_v(k)/d\Omega = r_0^2 |1 + P_v(k) + P_v(-k)|^2 (\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}')^2$$

where r_0 is the classical radius of the electron, $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}'$ are polarization vectors for the incident and scattered photon, k is the photon energy in a.u., and

$$[2] \quad P_v(k) = \frac{1}{3} \sum_n \frac{\langle \phi_0(r_1, r_2) | \mathbf{p}_1 + \mathbf{p}_2 | \phi_n(r_1, r_2) \rangle \cdot \langle \phi_n(r_1, r_2) | \mathbf{p}_1 + \mathbf{p}_2 | \phi_0(r_1, r_2) \rangle}{E_0 - E_n + k}$$

where E_0 is the energy of the ground state, E_n the energies of the intermediate states, $\phi_0(r_1, r_2)$ designates the ground state of H^- , and $\phi_n(r_1, r_2)$ the excited states. Alternatively, the differential elastic cross section in the dipole length formalism can be written as

$$[3] \quad d\sigma_L(k)/d\Omega = r_0^2 k^4 |P_L(k) + P_L(-k)|^2 (\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}')^2$$

where

$$[4] \quad P_L(k) = \frac{1}{3} \sum_n \frac{\langle \phi_0(r_1, r_2) | \mathbf{r}_1 + \mathbf{r}_2 | \phi_n(r_1, r_2) \rangle \cdot \langle \phi_n(r_1, r_2) | \mathbf{r}_1 + \mathbf{r}_2 | \phi_0(r_1, r_2) \rangle}{E_0 - E_n + k}$$

Consider the dipole velocity formulation first. Equation 2 may be rewritten as

$$[5] \quad P_V(k) = (1/3) \langle \phi_0(r_1, r_2) | (\mathbf{p}_1 + \mathbf{p}_2) \cdot \Psi_V(r_1, r_2) \rangle$$

where

$$[6] \quad \Psi_V(r_1, r_2) = \sum_n \frac{|\phi_n(r_1, r_2)\rangle \langle \phi_n(r_1, r_2) | \mathbf{p}_1 + \mathbf{p}_2 | \phi_0(r_1, r_2) \rangle}{E_0 - E_n + k}$$

$\Psi_V(r_1, r_2)$ is the solution of the differential equation

$$[7] \quad [E_0 - H + k] \Psi_V(r_1, r_2) = (\mathbf{p}_1 + \mathbf{p}_2) | \phi_0(r_1, r_2) \rangle$$

and

$$[8] \quad H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}$$

From [7] the following result is obtained

$$[9] \quad \int \Psi_{1s}(r_2) [E_0 - H + k] \Psi_V(r_1, r_2) d\tau_2 = \int \Psi_{1s}(r_2) (\mathbf{p}_1 + \mathbf{p}_2) \phi_0(r_1, r_2) d\tau_2$$

where the asymptotic approximation is introduced as

$$[10, 11] \quad \lim_{r_1 \rightarrow \infty} \phi_0(r_1, r_2) = \chi(r_1) \Psi_{1s}(r_2); \quad \chi(r_1) = \frac{N e^{-\gamma r_1}}{r_1}$$

and N is a normalization constant, $\gamma = (2E)^{1/2}$, and E is the binding energy. Equation 9 may be reexpressed as

$$[12] \quad \theta_V(r_1) [E_0 - E_{1s} + k] + (1/2) \nabla_1^2 \theta_V(r_1) = \mathbf{p}_1 \chi(r_1)$$

where E_{1s} is the ground state energy of the hydrogen atom and

$$[13] \quad \theta_V(r_1) = \int \Psi_{1s}(r_2) \Psi_V(r_1, r_2) d\tau_2$$

Expressing $\theta_V(r)$ in the form

$$[14] \quad \theta_V(r) = \hat{r} \chi(r) g_V(r) r^n$$

leads to the differential equation

$$[15] \quad g_V''(r) + 2g_V'(r) [(n/r) - \gamma] + g_V(r) [2k - (2n\gamma/r) + (n^2 - n - 2)/r^2] = 2r^{-n} \chi(r)^{-1} \hat{r} \cdot \mathbf{p} \chi(r)$$

The choice $n = -1$ simplifies [15] to

$$[16] \quad r g_V''(r) - 2[1 + \gamma r] g_V'(r) + [2kr + 2\gamma] g_V(r) = 2ri(1 + \gamma r)$$

which can be solved by taking the Laplace transform, $G_V(s) = \int_0^\infty e^{-sr} g_V(r) dr$. The resulting differential equation is solved to give

$$[17] \quad [s^2 - 2\gamma s + 2k] G_V(s) = - \int 2i(2\gamma s^{-3} + s^{-2})(s^2 - 2\gamma s + 2k) ds + 2i\lambda$$

where λ is an arbitrary integration constant. Now

$$[18] \quad G_V(s) = 2is^{-2} [s^2 - 2s\gamma + 2k]^{-2} [-s^3 + \lambda s^2 + (2k - 4\gamma^2)s + 2k\gamma]$$

from which $g_V(r)$ can be determined to be

$$[19] \quad g_V(r) = f(r; l, m) + f(r; l \rightarrow m, m \rightarrow l)$$

where

$$[20] \quad f(r; l, m) = (l - m)^{-3} e^{lr} \{ a(l^2 r - lmr - l - m) + b(lr - mr - 2) + cl^{-2}(l^2 r - lmr - 3l + m) + dl^{-3}(l^2 r - lmr - 2m - 4l) \} + (1/2)l^{-2}m^{-2}c + dl^{-3}m^{-3}(l + m - (1/2)rlm)$$

and $f(r; l \rightarrow m, m \rightarrow l)$ signifies the interchange of l and m , which are the roots of the equation $s^2 - 2\gamma s + 2k = 0$, and the constants a, b, c , and d are respectively $-2i, 2i\lambda, 4ik - 8i\gamma^2$, and $4ik\gamma$.

The factor $P_V(k)$ is then determined from the expression

$$[21] \quad P_V(k) = \frac{-8\pi i N^2}{3} \int_0^\infty e^{-2\gamma r} (\gamma r^{-1} + r^{-2}) g_V(r) dr$$

From the functional form of $g_V(r)$ it is apparent that $P_V(k)$ is divergent. Furthermore there is no choice for the arbitrary constant λ which removes this divergence.

To contrast the situation for the dipole velocity formulation with the dipole length situation, we outline the calculation of $P_L(k)$ which proceeds along similar lines. Defining

$$[22] \quad \Psi_L(r_1, r_2) = \sum_n \frac{|\phi_n(r_1, r_2)\rangle \langle \phi_n(r_1, r_2)| r_1 + r_2 | \phi_0(r_1, r_2)\rangle}{E_0 - E_n + k}$$

allows $P_L(k)$ to be written as

$$[23] \quad P_L(k) = (1/3) \langle \phi_0(r_1, r_2) | (r_1 + r_2) \cdot \Psi_L(r_1, r_2) \rangle$$

Now $\Psi_L(r_1, r_2)$ satisfies the differential equation

$$[24] \quad [E_0 - H + k] \Psi_L(r_1, r_2) = (r_1 + r_2) \phi_0(r_1, r_2)$$

From [24] we obtain the result

$$[25] \quad \theta_L(r_1) [E_0 - E_{1s} + k] + (1/2) \nabla_1^2 \theta_L(r_1) = r_1 \chi(r_1)$$

where

$$[26] \quad \theta_L(r_1) = \int \Psi_{1s}(r_2) \Psi_L(r_1, r_2) d\tau_2$$

and

$$[27] \quad E_0 - E_{1s} + k = k - (1/2)\gamma^2$$

On writing

$$[28] \quad \theta_L(r) = \hat{r} \chi(r) g_L(r) r^n$$

converts [25] into the following differential equation

$$[29] \quad g_L''(r) + 2\left(\frac{n}{r} - \gamma\right) g_L'(r) + \left(2k - \frac{2n\gamma}{r} + \frac{n^2 - n - 2}{r^2}\right) g_L(r) = 2r^{1-n}$$

which for the choice $n = -1$ can be solved by taking the Laplace transform. The solution of the resulting equation is

$$[30] \quad G_L(s) = [\frac{1}{2}s^2 - \gamma s + k]^{-2} [\int s^{-4} (-\frac{1}{2}s^2 + \gamma s - k) ds + \lambda']$$

where the arbitrary constant λ' can be selected such that the singularity at $s = \gamma + (\gamma^2 - 2k)^{1/2}$ is removed. $P_L(k)$ is then obtainable directly from the Laplace transform, $G_L(s)$, as

$$[31] \quad P_L(k) = (8\pi N^2/3) G_L(2\gamma)$$

which is well behaved for all k .

Discussion

The inequivalence of the dipole length and dipole velocity results arises from the use of an approximate eigenstate, the asymptotic wavefunction, of the correct Hamiltonian. The asymptotic

approximation for $\phi_0(r_1, r_2)$ is an eigenstate of the Hamiltonian only for the $\lim r_2 \rightarrow \infty$. When this approximate eigenstate is employed in evaluating matrix elements for all r , the dipole length formulation deemphasizes the small r region, since the r^{-1} behavior at the origin (arising from $\phi_0(r_1, r_2)$) is cancelled by the r^2 from the volume element. The dipole velocity formalism emphasizes the region of small r , to the extent that the differential elastic cross section becomes singular. The divergence of the differential scattering cross section would be strongest for the case of the dipole acceleration formulation. This is due to the fact that the dipole acceleration operator places greater emphasis on the small r region, compared with the dipole velocity and dipole length operators.

Although divergences of the type obtained for the differential elastic scattering cross section in the dipole velocity formulation may be generally appreciated, when asymptotic wave functions are employed, it does not appear to have been explicitly demonstrated. The appearance of a divergent result is not at all obvious from an examination of the appropriate transition matrix element. Taking a representation of the p wave radial wavefunction for the H^- ion continuum states of the form (Geltman 1956)

$$[32] \quad \eta(r) = \begin{cases} N' r^2 e^{-\gamma r} F_1(2 - t^{-1}; 4; 2tr), & r \leq R_0 \\ \frac{\sin(\kappa r + \delta)}{\kappa r} - \cos(\kappa r + \delta), & r \geq R_0 \end{cases}$$

where N' is a matching constant, δ the phase shift, $t = (2R_0^{-1} - 2E_\kappa)^{1/2}$, and R_0 the radius of the well, leads to the following transition matrix element,

$$\int_0^{R_0} r^2 \{e^{-\gamma r} F_1(2 - t^{-1}; 4; 2tr)\} \frac{\partial}{\partial r} \{r^{-1} e^{-\gamma r}\} dr + \int_{R_0}^{\infty} r^2 \left\{ \frac{\sin(\kappa r + \delta)}{\kappa r} - \cos(\kappa r + \delta) \right\} \frac{1}{r} \frac{\partial}{\partial r} \{r^{-1} e^{-\gamma r}\} dr$$

which is not divergent. It is necessary to examine the total sum over states directly. It is of course very easy to choose an approximation for the continuum wave functions which would create a singular transition matrix element; however, this is to a certain extent a moot point, since the derivation employed in this paper does not specify the functional form of the intermediate continuum states. However a simple *approximate* argument is available for exhibiting the divergent character of $P_V(k)$ in the asymptotic approximation.¹ By invoking an average energy approximation for the denominator of [2], $E_0 - E_n \approx \Delta E$, then [2] can be expressed in the form

$$[33] \quad P_V(k) \approx (\Delta E + k)^{-1} \langle \phi_0(r_1, r_2) | (\mathbf{p}_1 + \mathbf{p}_2)^2 | \phi_0(r_1, r_2) \rangle$$

which is very easily shown to be divergent, when the asymptotic approximation is employed.

The outcome of this paper is thus to provide a clear choice between the dipole length, dipole velocity, and dipole acceleration formulations, when asymptotic type wave functions are employed for the calculation of the differential elastic scattering cross section and related properties. The dipole length formulation is the appropriate choice, since it weights the small r region least heavily of the three possibilities.

¹Adelman, S.A. 1974. Private communication.

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