Reduced Green's Function for the Ground State of the Hydrogen Atom

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The reduced Coulomb Green's function for the ground state of the one-electron atom is obtained in closed form by direct solution of the relevant differential equation.

Recently, there has been some interest in the reduced Coulomb Green's function for the ground state of the one-electron atom. Hameka[1] has obtained a Legendre expansion of this function, and Hostler[2] has given a closed-form expression. Both Hameka and Hostler obtained their expressions for the reduced Green's function by applying appropriate limiting procedures to the corresponding expression for the full Coulomb Green's function. There is a much simpler alternative approach which yields the reduced Green's function directly as the solution of a differential equation and this approach will be outlined here.

The reduced Green's function for the ground state of a one-electron atom with nuclear charge Z is the solution of the equation, in atomic units

$$(\nabla_1^2 + 2Z/r_1 - Z^2)G^1(\vec{r}_1, \vec{r}_2)$$
$$= \delta^3(\vec{r}_1 - \vec{r}_2) - (Z^3/\pi)e^{-Z(r_1+r_2)} \qquad (1)$$

together with suitable regularity conditions at the origin and at infinity. Rotational invariance and uniqueness require that $G^1(\vec{r}_1, \vec{r}_2)$ depend only on r_1, r_2, and $r_{12} = |\vec{r}_1 - \vec{r}_2|$. Symmetry requires that $G^1(\vec{r}_1, \vec{r}_2)$ be symmetric in r_1 and r_2. The reduced Green's function is unique except for an arbitrary multiple of the homogenous solution of (1), and this may be fixed by requiring $G^1(\vec{r}_1, \vec{r}_2)$ be orthogonal to that homogenous solution.

We partition $G^1(\vec{r}_1, \vec{r}_2)$ into two parts

$$G^1(\vec{r}_1, \vec{r}_2) = g^1(|\vec{r}_1 - \vec{r}_2|) + F(\vec{r}_1, \vec{r}_2) \qquad (2)$$

such that $g^1(|\vec{r}_1 - \vec{r}_2|)$ satisfies the equation

$$(\nabla_1^2 - Z^2)g^1(|\vec{r}_1 - \vec{r}_2|) = \delta^3(\vec{r}_1 - \vec{r}_2). \qquad (3)$$

The solution of this equation is well known and is

$$g^1(r_{12}) = -(4\pi)^{-1}e^{-Zr_{12}}/r_{12}, \qquad (4)$$

and thus the equation for $F(\vec{r}_1, \vec{r}_2)$ becomes

$$(\nabla_1^2 + 2Z/r_1 - Z^2)F(r_1, r_2, r_{12})$$

$$= -(Z^3/\pi)e^{-Z(r_1+r_2)}$$
$$+ (Z/2\pi)e^{-Zr_{12}}/r_1 r_{12}. \qquad (5)$$

We now put

$$F(r_1, r_2, r_{12}) = (Z/\pi)e^{-Z(r_1+r_2)}f(r_1, r_2, r_{12}),$$

and express the resulting equation for $f(r_1, r_2, r_{12})$ in terms of the variables[3]

$$u = Z(r_1 + r_2 + r_{12}), \quad \text{and} \quad v = Z(r_1 + r_2 - r_{12}), \qquad (6)$$

finally obtaining

$$[D(u) - D(v)]f(u, v, r_2)$$
$$= \tfrac{1}{2}e^v - \tfrac{1}{4}(u^2 - 2r_2 u) + \tfrac{1}{4}(v^2 - 2r_2 v),$$
$$D(x) = e^x\left(\frac{\partial}{\partial x}e^{-x}(x^2 - 2r_2 x)\frac{\partial}{\partial x}\right). \qquad (7)$$

The form of (7) suggests that we look for solutions which are sumseparable and so we write $f(u, v, r_2)$ in the form

$$f(u, v, r_2) = U(u, r_2) + V(v, r_2) + c, \qquad (8)$$

where $U + V$ is a particular solutions of (7) satisfying the regularity conditions at the origin and at infinity, and c is a constant to be determined by the orthogonality condition on $G^1(\vec{r}_1, \vec{r}_2)$. It is now a simple matter to show that

$$U = \tfrac{1}{4}u + \tfrac{1}{2}\ln u, \quad \text{and} \quad V = \tfrac{1}{4}v - \tfrac{1}{2}\int_0^v \frac{e^t - 1}{t}dt \qquad (9)$$

form a permissible particular solution of (7), and to determine c. The latter task is facilitated by the observation that $G^1(\vec{r}_1, 0)$ must be orthogonal to e^{-Zr_1} and using this fact we are led to the value $c = \tfrac{1}{2}\gamma - \tfrac{5}{4}$ where γ is the Euler-Mascheroni constant. The resulting expression for $G^1(\vec{r}_1, \vec{r}_2)$ is

$$G^1(\vec{r}_1, \vec{r}_2) = -\frac{1}{4\pi} \frac{e^{-Zr_{12}}}{r_{12}} + \frac{Z}{2\pi} e^{-Z(r_1+r_2)}$$

$$\times \left(\gamma - \tfrac{5}{2} + Z(r_1+r_2) + \ln Z(r_1+r_2+r_{12})\right.$$

$$\left. - \int_0^{Z(r_1+r_2-r_{12})} \frac{e^t-1}{t} dt\right) \quad (10)$$

in agreement with the result derived by Hostler.[2]

[1] H. F. Hameka, J. Chem. Phys. 47, 2728 (1967); 48, 4810 (1968).

[2] L. C. Hostler, Phys. Rev. 178, 126 (1969).

[3] These variables are also of importance for the full Coulomb Green's function as shown by L. C. Hostler and R. H. Pratt, Phys. Rev. Letters 10, 469 (1963).

Photodetachment Cross Section of the Negative Ion of Lithium

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The photodetachment cross section for the negative ion of lithium is calculated following Geltman using an improved value of the electron affinity (0.62 eV) obtained by Weiss.

The photodetachment cross section of the negative ion of lithium was calculated by Geltman[1] employing a value 0.384 eV for the electron affinity of the lithium atom (or the binding energy of the negative lithium ion). This value was obtained by Geltman by extrapolating along the isoelectronic sequence and seemed to be considerably smaller than various other theoretical determinations. Thus, Moiseiwitsch[2] obtained 0.74 eV, Weiss[3] obtained 0.62 eV and Edlén[4] obtained 0.8 eV. Recently, experiments with electrically exploded lithium wires[5] indicated that the affinity of lithium is about 0.6 eV, close to the value calculated by Weiss.[3] The latter's method of calculation seems to be the most direct and elaborate and since it best agrees with the experiment, it will be adopted here as the best value of the electron affinity of lithium. A revised calculation of the photodetachment cross section seems appropriate. The much larger value of electron affinity, as compared with that of Geltman, would shift the photodetachment threshold and the continuum associated with the inverse process to much shorter wavelengths of the spectrum.

The photodetachment cross section of Li⁻ has not been measured. However, Geltman's calculations, as applied to the hydrogen negative ion, yielded good agreement with other methods and with the experiment. It can, thus, be expected that following the simple procedure employed by Geltman and using an improved value of the electron affinity would give reliable results.

It is assumed that the lithium (and the hydrogen) negative ion has only one bound state and therefore the total absorption coefficient (per unit density of negative ions) and the photodetachment cross section coincide. A further assumption is that the two $1s$ electron merge with the nucleus or that the lithium negative ion is likened to a hydrogen negative ion with the two electrons in the $2s$ orbital.

Geltman constructs eigenfunctions out of bound and free one-electron functions and assumes the potential in the one-electron Schrödinger equation to be a cutoff Coulomb potential

$$V(r) = 1/r_0 - 1/r, \quad r \le 0$$
$$= 0, \quad r \ge 0. \quad (1)$$

The potential is chosen such as to give one bound state of energy equal to the electron affinity of the neutral atom. The choice of functions assures the fulfillment of certain necessary conditions on the absorption coefficient[1] but not that of minimal energy. The photodetachment cross section is then obtained as

$$\sigma(k) = \tfrac{1}{3}(32\pi^2)\alpha a_0^2 (k_0^2 + k^2)/k$$