Relativistic correction to the dipole polarizability of a hydrogenic ion

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Abstract. The first relativistic correction of order α^2 to the dipole polarizability of a hydrogenic ion has been investigated by using mean excitation energy of the ion within the second-order perturbation theory. The density-dependent mean excitation energy is estimated via Bethe theory for the stopping cross section for a moving point charge interacting with the hydrogenic ion. In this approach only the unperturbed Dirac wavefunctions are required to evaluate the appropriate matrix elements. The first relativistic correction turns out to be $-(13/12)(\alpha Z)^2$. This has the correct sign and is within 5% of the exact result which is $-(28/27)(\alpha Z)^2$.

1. Introduction

The electric dipole polarizability α_d of an atom represents the simplest linear response of the electronic charge cloud to an electric field. It determines the most important term in the asymptotic behaviour of electron–atom interaction in the low energy collisions [1]. In electrostatics, it is closely related to dielectric constant [2] and it is also a measure of the Stark shift of energy levels. In optics, it is useful in the analysis of refraction and scattering of light, and of the electrical birefringence [3]. It is of interest to know the relativistic correction due to Dirac nature of the electron cloud. This can improve the accuracy of the coefficient in the intermolecular potentials [4, 5].

The dipole polarizability is given by [6]

$$\alpha_d = 2\left(\psi_1^{(1)}, \sum_{i=1}^{N} r_i P_1(\cos\theta_i)\psi_0 \right) \tag{1}$$

where ψ_0 is the unperturbed ground state wave function, $\psi_1^{(1)}$ is the first-order perturbed wave function, N is the number of electrons in the system. For one-electron systems, $\psi_1^{(1)}$ can be calculated exactly by the method of Dalgarno and Lewis [7] in which the perturbed wave function satisfies an inhomogeneous differential equation. For H atom, the non-relativistic value of $\alpha_d = 4\cdot5$. When the perturbation theory is applied for the relativistic calculation of α_d, the calculation is quite complicated even for H atom. For atoms other than H, or for a Coulomb potential perturbed by other central potentials, the calculation becomes severely complicated.

There are several calculations of relativistic corrections to α_d for H atom. A general theory [8] of electromagnetic polarizabilities of composite system described by

infinite-component wave equation has been developed and applied to the relativistic H atom which is described completely by an O(4, 2) infinite-component wave equation. The method of Dalgarno and Lewis [7] has been used [9] to obtain the relativistic α_d for an H atom. Several calculations using the method of Coulomb's Green function [10, 11] have been performed for the relativistic calculation of α_d for H atom. In one calculation [12], only the Darwin Hamiltonian was taken into account which produced wrong results. Kaneko [13] showed that the explicit solution of the perturbed Dirac equation is not necessary to calculate the exact values of the corrections.

2. Theory

By expressing $\psi_1^{(1)}$ over a complete set of unperturbed eigenstates, we get

$$\alpha_d = 2 \sum_{n \neq 0} \frac{|(\psi_n \sum_{i=1}^N r_i P_1(\cos\theta_i)\psi_0)|^2}{E_n - E_0}. \tag{2}$$

The summation is over all intermediate states including the continuum. Equation (2) requires a complete knowledge of the spectrum of the atomic system. A useful approach is to replace $E_n - E_0$ by a mean excitation energy Δ, and making use of the completeness relation

$$\sum_{n=0} |\psi_n\rangle\langle\psi_n| = 1, \tag{3}$$

we now get

$$\alpha_d = \frac{2}{\Delta} \left[\left(\psi_0, \sum_{i=1}^N r_i^2 P_1^2(\cos\theta_i)\psi_0 \right) - \left(\psi_0, \sum_{i=1}^N r_i P_1(\cos\theta_i)\psi_0 \right)^2 \right]. \tag{4}$$

If Δ is taken to be equal to the ionization potential then α_d comes out to be correct within an order of magnitude [6].

In the present work, we show that Δ can be connected to the electron density $\rho(r)$. The stopping cross section S for a high-speed point charge penetrating through a homogeneous electron gas is given by [14, 15]

$$S = K \frac{\ln E}{E} \ln \Delta \tag{5}$$

where K is a constant, E is the energy of the penetrating charge and

$$\ln \Delta = \int d^3 r \rho(r) \ln \omega_p(r) \tag{6}$$

with $\omega_p(r)$ being the plasma frequency of the medium which is given by

$$\omega_p(r) = (4\pi\rho(r)z)^{1/2} \tag{7}$$

where $z = Z - N + 1$, is the residual charge of the electron gas which has nuclear charge Z and N electrons.

We now apply (4) with the definition of Δ given by (6) to calculate α_d for a hydrogenic ion in the ground state.

We can now write

$$\alpha_d = \frac{2}{3\Delta} \langle r^2 \rangle. \tag{8}$$

The relativistic charge density of a hydrogenic ion is [16]

$$\rho(r) = \frac{(2Z)^3(1+\gamma_1)e^{-2Zr}(2Zr)^{(2\gamma_1-2)}}{4\pi(1+\varepsilon_1)\Gamma(2\gamma_1+1)} \tag{9}$$

where

$$\gamma_1 = (1-\alpha^2Z^2)^{1/2}$$

and

$$\varepsilon_1 = \left[1+\left(\frac{\alpha Z}{\gamma_1}\right)^2\right]^{-1/2}. \tag{10}$$

α is the fine-structure constant.

With $\rho(r)$ given by (9), we obtained all the relevant integrals analytically [17] and got the following expressions for $\langle r^2 \rangle$ and $\ln \Delta$

$$\langle r^2 \rangle = \frac{(1+\gamma_1)\Gamma(2\gamma_1+3)}{4Z^2(1+\varepsilon_1)\Gamma(2\gamma_1+1)} \tag{11}$$

$$2\ln\Delta = \ln(4\pi Z) + \frac{(1+\gamma_1)}{(1+\varepsilon_1)}\left[\ln\frac{(2Z)^3(1+\gamma_1)}{4\pi(1+\varepsilon_1)\Gamma(2\gamma_1+1)}\right.$$
$$\left. -(2\gamma_1+1)+(2\gamma_1-2)\psi(2\gamma_1+1)\right] \tag{12}$$

where

$$\psi(2\gamma_1+1) = -C + \sum_{n=0}^{\infty}\left(\frac{1}{n+1}-\frac{1}{2\gamma_1+1+n}\right) \tag{13}$$

with $C = 0.577215\cdots$ as the Euler's constant.

Now we expand γ_1, ε_1 and their functions up to terms of order $(\alpha Z)^2$, after some algebra, we obtain

$$\langle r^2 \rangle = \frac{3}{Z^2}\left[1-\frac{7}{12}(\alpha Z)^2\right] \tag{14}$$

and

$$\Delta = 2Z^2\exp\left(-\frac{3}{2}+\frac{1}{2}\alpha^2Z^2\right). \tag{15}$$

We finally obtain α_d correct to order $(\alpha Z)^2$.

$$\alpha_d = \frac{e^{3/2}}{Z^4}\left[1-\frac{13}{12}(\alpha Z)^2\right]. \tag{16}$$

3. Results

The first term in (16) yields the non-relativistic value with the correct Z dependence. Our non-relativistic value of H atom is 4·4817 against the exact value of 4·50. The

second term gives the first-order relativistic correction. Our coefficient 13/12 is within five per cent of the exact value 28/27 given by Kaneko [13], who did a perturbation calculation by use of the Dirac equation. The negative sign indicates relativistic contraction of the mean radius of the electron orbit. Feiock and Johnson [12] obtained a positive sign for their first-order relativistic correction because they employed incorrect first-order perturbed wave function.

Though our calculations presented here are much simpler than other calculations present in the literature, yet they yield quite accurate results. The same formalism, which requires only the unperturbed density, can be applied to Coulomb potentials perturbed by more complex potentials.

References

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