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ELEMENTARY PARTICLE PHYSICS AND FIELD THEORY

CALCULATION OF THE SCREENING CONSTANT AND ENERGY OF A TWO-ELECTRON ATOM

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Using the results of a paper previously published by the author, general expressions have been obtained for the energy and screening constant for a two-electron atom for arbitrary sets of quantum numbers of the electrons. In the particular case of the ground state of the atom, the well-known classical result is obtained from the general formulas.

Keywords: two-electron atom, arbitrary sets of quantum numbers, energy, screening constant.

INTRODUCTION

The most effective approach to solving the quantum-mechanical analog of the classical three-body problem, in this case, to calculate the energy of a two-electron atom is the Hylleraas variational method [1, 2] and its various modifications, including an increase in the number of variational parameters [3]. Applying this method to a calculation of the energy and the screening constant for the ground state of the helium atom with electrons in the states $\{n=1, l=0, m=0\}$ and $\{n'=1, l'=0, m'=0\}$ gives a result in agreement with experiment (see [4, 5]). It is of interest to extend this method to arbitrary states of the electrons in the general case of a two-electron atom with arbitrary value of Z (He, Li^+, etc.), including, as a special case, the ground state of the helium atom ($Z=2$), considered elsewhere. This then is the subject of discussion in the present paper. We will also apply the results of one of our previous papers [6].

1. INTERACTION OF ELECTRONS. CORRECTION TO THE ENERGY OF THE ATOM

The total energy E_{tot} of a two-electron atom is found by adding together the energies of the atomic electrons $E_{\text{at}} = E_n + E_{n'}$ in the field of the nucleus, these having the value

$$E_n = -\frac{(Z\alpha)^2 m_e c^2}{2n^2},\ n=1, 2, \ldots,\ \alpha = \frac{e^2}{\hbar c}, \tag{1}$$

together with the interaction energy of the electrons E_{ee}, this being, in general, a correction to E_{at}, but nevertheless comparable in magnitude with E_{at}, in which regard, in place of perturbation theory it has been proposed to use the variational method, which is applied next in Section 2 with the variational parameter Z' with the substitution $Z \to Z'$ in the wave functions, at the same time employing the general results of our previous paper [6] applied to the problem at

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hand.

The value of E_{ee}, as is well known [4, 5], is equal to (the plus and minus signs refer to the singlet and triplet states)

$$E_{ee}^{(\pm)} = K \pm J\,, \tag{2}$$

where K is the average Coulomb interaction energy:

$$K = e^2 \int dV \left|\Psi_M(\boldsymbol{r})\right|^2 \int dV' \left|\Psi_{M'}(\boldsymbol{r}')\right|^2 \frac{1}{\left|\boldsymbol{r}-\boldsymbol{r}'\right|}\,, \tag{3a}$$

and J is the so-called exchange energy, which does not have a classical analog:

$$J = e^2 \int dV\ \Psi_M(\boldsymbol{r})\ \Psi_{M'}^{*}(\boldsymbol{r}) \int dV'\ \Psi_M^{*}(\boldsymbol{r}')\ \Psi_{M'}(\boldsymbol{r}') \frac{1}{\left|\boldsymbol{r}-\boldsymbol{r}'\right|}\,. \tag{3b}$$

The symbols $M = \{n,l,m\}$ and $M' = \{n',l',m'\}$ are used here for brevity to denote sets of quantum numbers of the electrons, and the electron wave function in the field of the nucleus (Ze) is equal to [5]

$$\Psi_M \equiv \Psi_{nlm} = R_{nl}\ P_{lm}\ \Phi_m\,. \tag{4}$$

The factored dependence on the spherical coordinates is given by the expressions

$$R_{nl} \equiv R_{nl}(r) = r_0^{-3/2} R_{nl}(\rho)\,,\ r_0 = \frac{\hbar^2}{m_e\left(Ze^2\right)}, \tag{5a}$$

$$R_{nl}(\rho) = C_{nl}\ e^{-\frac{\rho}{n}} \left(\frac{2\rho}{n}\right)^l F\left(-n+l+1, 2l+2, \frac{2\rho}{n}\right),\ \rho = \frac{r}{r_0}\,, \tag{5b}$$

$$C_{nl} = \frac{2}{n^2(2l+1)!}\sqrt{\frac{(n+l)!}{(n-l-1)!}}\,, \tag{5c}$$

$$\int_0^\infty R_{nl}(r)\ R_{n'l}(r)\ r^2 dr = \int_0^\infty R_{nl}(\rho)\ R_{n'l}(\rho)\ \rho^2 d\rho = \delta_{nn'} \tag{5d}$$

(F is the degenerate hypergeometric function and $\delta_{nn'}$ is the Kronecker symbol),

$$P_{lm} \equiv (-1)^m\ P_{lm}(\cos\theta)\,, \tag{6a}$$

$$P_{lm}(x) = \sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}}\ \left(1-x^2\right)^{\frac{m}{2}} \frac{d^{l+m}}{dx^{l+m}}\left[\frac{\left(x^2-1\right)^l}{2^l l!}\right], \tag{6b}$$

$$\int_{-1}^{1} P_{lm}(x)\, P_{l'm}(x)dx = \delta_{ll'} \tag{6c}$$

($P_{lm}(x)$ are the normalized adjoint Legendre polynomials),

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}, \tag{7a}$$

$$\int_{0}^{2\pi} \Phi_m{}^*(\varphi)\Phi_{m'}(\varphi)d\varphi = \delta_{mm'}. \tag{7b}$$

For convenience in what follows, it is useful to transform in expressions (3a) and (3b) into dimensionless variables and functions:

$$K = \alpha(Z\alpha)m_e c^2\, \tilde{K}, \tag{8}$$

$$\tilde{K} = \int d\tilde{V} \left|\tilde{\Psi}_M(\boldsymbol{\rho})\right|^2 \int d\tilde{V}' \left|\tilde{\Psi}_{M'}(\boldsymbol{\rho}')\right|^2 \frac{1}{|\boldsymbol{\rho}-\boldsymbol{\rho}'|}, \tag{8a}$$

$$J = \alpha(Z\alpha)m_e c^2\, \tilde{J}, \tag{9}$$

$$\tilde{J} = \int d\tilde{V}\, \tilde{\Psi}_M(\boldsymbol{\rho})\, \tilde{\Psi}_{M'}{}^*(\boldsymbol{\rho}) \int d\tilde{V}'\, \tilde{\Psi}_M{}^*(\boldsymbol{\rho}')\, \tilde{\Psi}_{M'}(\boldsymbol{\rho}') \frac{1}{|\boldsymbol{\rho}-\boldsymbol{\rho}'|}. \tag{9a}$$

Here we have introduced the notation $\boldsymbol{\rho} = \boldsymbol{r}/r_0$ and $d\tilde{V} = dV/r_0{}^3$, and the functions $\tilde{\Psi}_M$ differ from the functions Ψ_M (Eqs. (4) and (5a)–(5d)) by the substitution $R_{nl}(r) \to R_{nl}(\rho)$ with the factor $r_0{}^{-3/2}$ dropped.

Thus, employing representation (4) of these functions with equalities (5a), (6a), and (7a) taken into account, we obtain

$$\tilde{K} = \int_0^\infty d\rho\, \rho^2\, R_{nl}{}^2(\rho) \int_0^\infty d\rho'\, \rho'^2\, R_{n'l'}{}^2(\rho') \int_{-1}^{1} d\cos\theta\, P_{lm}{}^2(\cos\theta) \int_{-1}^{1} d\cos\theta'\, P_{l'm'}{}^2(\cos\theta')$$

$$\times \frac{1}{2\pi} \int_0^{2\pi} d\varphi\, \frac{1}{\sqrt{\rho^2+\rho'^2-2\rho\rho'(\sin\theta\sin\theta'\cos\varphi+\cos\theta\cos\theta')}}, \tag{10}$$

$$\tilde{J} = \int_0^\infty d\rho\, \rho^2\, R_{nl}(\rho)\, R_{n'l'}(\rho) \int_0^\infty d\rho'\, \rho'^2\, R_{nl}(\rho')\, R_{n'l'}(\rho') \int_{-1}^{1} d\cos\theta\, P_{lm}(\cos\theta)$$

$$\times P_{l'm'}(\cos\theta) \int_{-1}^{1} d\cos\theta'\, P_{lm}(\cos\theta')\, P_{l'm'}(\cos\theta') \tag{11a}$$

$$\times \frac{1}{(2\pi)^2} \int_0^{2\pi} d\varphi \int_0^{2\pi} d\varphi' \frac{\exp[i(m-m')(\varphi-\varphi')]}{\sqrt{\rho^2+\rho'^2-2\rho\rho'[\sin\theta\sin\theta'\cos(\varphi-\varphi')+\cos\theta\cos\theta']}}.$$

If we employ the Euler formula $e^{ix} = \cos x + i\sin x$, it is easy to see that the imaginary part of expression (11a) in any case ($m \neq m'$, or $m = m'$) vanishes, as it should, i.e., it is possible to make the replacement $\exp[i(m-m')(\varphi-\varphi')] \rightarrow \cos[(m-m')(\varphi-\varphi')]$, so that we obtain, in analogy with the representation of $\tilde{K}$ (Eq. (10)),

$$\tilde{J} = \int_0^{\infty} d\,\rho\,\rho^2\, R_{nl}(\rho)\, R_{n'l'}(\rho) \int_0^{\infty} d\,\rho'\,\rho'^2\, R_{nl}(\rho')\, R_{n'l'}(\rho') \int_{-1}^{1} d\cos\theta\, P_{lm}(\cos\theta)\, P_{l'm'}(\cos\theta)$$

$$\times \int_{-1}^{1} d\cos\theta'\, P_{lm}(\cos\theta')\, P_{l'm'}(\cos\theta') \frac{1}{2\pi} \int_0^{2\pi} d\varphi \frac{\cos[(m-m')\varphi]}{\sqrt{\rho^2+\rho'^2-2\rho\rho'(\sin\theta\sin\theta'\cos\varphi+\cos\theta\cos\theta')}}. \quad (11b)$$

To obtain equalities (10) and (11b), we observed that the double integral $\int_0^{2\pi} d\varphi \int_0^{2\pi} d\varphi'$ over spherical coordinates, for example, in expression (11b), reduces to $\int_0^{2\pi} d\varphi$ since the integrand depends only on the difference $\varphi - \varphi'$ (denoted after the substitution of variables $\varphi - \varphi' \rightarrow \varphi$ as φ with subsequent dummy integration over $d\varphi'$, giving the factor 2π), where the limits of integration do not vary (see in this regard [7]).

2. THE VARIATIONAL METHOD: ENERGY OF A TWO-ELECTRON ATOM AND THE SCREENING CONSTANT

For convenience in what follows, we introduce the following notation. The total average kinetic energy $\mathrm{T}_\Sigma = \mathrm{T}' + \mathrm{T}$ of the electrons in a two-electron atom expressed in terms of the variational parameter Z' can be written in the form

$$\mathrm{T}_\Sigma = \mathrm{T}_E\, Z'^2, \quad (12)$$

$$\mathrm{T}_E = \left(\frac{1}{n'^2} + \frac{1}{n^2}\right) \frac{\alpha^2 m_e c^2}{2}, \quad (12a)$$

which follows from a result in our previous paper [6], according to which $\mathrm{T}_\Sigma = |E_{n'}| + |E_n|$ for arbitrary sets of quantum numbers. With this notation (Eq. (12a)), the average total potential energy of the electrons in the field of the nucleus, expressed as a function of the variational parameter, according to a result of that same paper, is equal to

$$\Pi_\Sigma = -2\,\mathrm{T}_E\, ZZ'. \quad (12b)$$

In line with the notation introduced above, the energy $E(Z') = \mathrm{T}_\Sigma + \Pi_\Sigma + E_{ee}^{(\pm)}$ of a two-electron atom expressed as a function of the parameter Z' with equalities (2), (8), (9), (12a), and (12b) taken into account, can be written in the form

$$E(Z') = \mathrm{T}_E \{Z'^2 - 2ZZ' + I^{(\pm)} Z'\}, \tag{13}$$

where

$$I^{(\pm)} = \frac{E_{ee}^{(\pm)}}{Z'\mathrm{T}_E} \equiv 2\frac{\tilde{K} \pm \tilde{J}}{\tilde{\mathrm{T}}_E}, \tag{13a}$$

and the value $\tilde{\mathrm{T}}_E$ differs from T_E (Eq. (12a)) by dropping the factor $\frac{\alpha^2 m_e c^2}{2}$.

Next, in accordance with the idea of the variational method [2, 3] (see also [4, 5]), the true value of the energy E_{real} of a two-electron atom corresponds to the value assigned by Eq. (13) at the minimum of this expression (for $Z' \to Z_{\text{eff}}$), i.e., $E_{\text{real}} = E(Z_{\text{eff}})$. Inserting this value at the minimum, i.e., in the relation obtained by setting $\frac{dE(Z')}{dZ'} = 0$, we obtain

$$Z_{\text{eff}} = Z - \sigma, \ \sigma = \frac{1}{2} I^{(\pm)} = \frac{\tilde{K} \pm \tilde{J}}{\tilde{\mathrm{T}}_E}, \tag{14}$$

and the value of the energy as a result of a simple calculation turns out to be

$$E_{\text{real}} = -\mathrm{T}_E (Z - \sigma)^2. \tag{15}$$

From a comparison with the energy of the atom $E_0 = -\mathrm{T}_E Z^2$ with the interaction energy of the electrons not taken into account, it follows that the quantity σ should be interpreted as a screening constant taking into account the mutual influence of the electrons, effectively decreasing the charge of the nucleus.

3. DISCUSSION

Formulas (10), (11a), (14), and (15), as has already been noted, are approximately valid within the framework of the variational method for arbitrary sets of quantum numbers of the electrons $\{n,l,m\}$ and $\{n'l',m'\}$. For illustrational purposes and to check the calculations, let us consider the particular case of the ground state of a two-electron atom with identical sets of quantum numbers of the electrons $\{1,0,0\}$.

As is well-known [4, 5], in this case only $\tilde{K}$ contributes to the energy. To transform the last integral in expression (10) (the integral over $d\varphi$) we note that the expression in parentheses in the radicand is simply $\cos\tilde{\theta}$, where $\tilde{\theta}$ is the angle between the vectors $\boldsymbol{r}$ and $\boldsymbol{r}'$ (ρ and ρ'). Next, choosing $\theta \equiv \tilde{\theta}$, we see that the integrand, taking the value $P_{00} = 1/\sqrt{2} = \text{const}$ into account, does not depend on θ' and φ, so that the integration over these variables is a dummy integration, giving a factor of 4π. Taking account the form of the function $R_{10}(\rho) = 2e^{-\rho}$ [5], subsequent integration is quite elementary (see also [4, 5]) and leads to the result $\tilde{K} = 5/8$. Observing that $\tilde{T}_E = (1/n^2 + 1/n'^2) = 2$ in the ground state, where $n = n' = 1$, we find, according to Eqs. (14), that $\sigma = 5/16$. These results are in agreement with the classical results presented in these same books.

Somewhat more cumbersome is the procedure of calculating the energy and the screening constant in the excited states of a two-electron atom with *energy* quantum numbers of the electrons $n' = 1$; $n = 2, 3, \ldots$ By virtue of its obvious importance for the helium atom, this will be the subject of future work, and we plan to publish the result separately.

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