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SOME ASYMPTOTIC FORMULAE FOR ONE-ELECTRON TWO-CENTER PROBLEM

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Asymptotic formulae of some expectation values related to the relativistic corrections in inverse powers of the internuclear distance R for the $1s\sigma_g$ electron state of hydrogen molecular ion H_2^+ and the $1s\sigma$ molecule-like state of antiprotonic helium atom $He^+\bar{p}$ are obtained with the use of the first-order perturbation function. Using these asymptotic formulae, the relativistic correction of order $m\alpha^6$ for these states in reciprocal powers of the internuclear distance R is derived to accuracy of $\mathcal{O}(R^{-4})$.

В первом порядке теории возмущений по обратным степеням большого расстояния R между ядрами получены асимптотические выражения для некоторых ожидаемых величин, относящихся к релятивистским поправкам для электронного $1s\sigma_g$-состояния молекулярного иона водорода H_2^+ и молекулоподобного $1s\sigma$-состояния атома антипротонного гелия $He^+\bar{p}$. Для таких состояний с помощью асимптотик выведены релятивистские поправки порядка $m\alpha^6$ в виде разложения по обратным степеням расстояния R с остаточным членом $\mathcal{O}(R^{-4})$.

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INTRODUCTION

The H_2^+ molecular ion is a simple example of one-electron two-center system. In the case of large internuclear distance R of this ion, the wave function and the electronic energy were found by many authors as earlier applications of wave mechanics [1–5]. Since this time, the electronic energy expansion in inverse powers of the internuclear distance R, with the coefficients expressed in terms of nuclear charges and separated atomic quantum numbers, was also found by many different authors [6–9]. In the present work our purposes are to derive the asymptotic formulae of some expectation values in inverse powers of internuclear distance R for the $1s\sigma_g$ electron state of H_2^+ molecular ion and the $1s\sigma$ molecule-like state of antiprotonic helium atom $He^+\bar{p}$ and to calculate analytically the relativistic correction of order $m\alpha^6$ for these states using the obtained asymptotic formulae. The relativistic corrections of orders $m\alpha^4$ and $m\alpha^6$ for the states had been calculated numerically for a wide range of R in [10, 11].

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1. ASYMPTOTIC FORMULAE FOR SOME EXPECTATION VALUES

In this section we will consider the evaluations of the expectation values of V, V^2 and $\mathbf{p}V\mathbf{p}$ through the first-order approximation.

Here V is the Coulomb potential of the system, and has the form:

$$V = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2}, \tag{1}$$

and the momentum operator for the electron is

$$\mathbf{p} = -i\left(\frac{\partial}{\partial r_1}\frac{\mathbf{r}_1}{r_1} + \frac{\partial}{\partial r_1}\frac{\mathbf{r}_2}{r_2}\right), \tag{2}$$

where r_1 and r_2 are the distances from an electron to nuclei 1 and 2, respectively.

In ordinary perturbation theory, the Schrödinger equation is

$$H\psi = E\psi, \tag{3}$$

where $H = H_0 + H'$ contains the unperturbed Hamiltonian H_0 and perturbation H'. Then we are looking for a solution of (3):

$$E = E_0 + E_1 + E_2 + \ldots, \tag{4}$$

$$\psi = \psi_0 + \psi_1 + \ldots \tag{5}$$

When internuclear distance R becomes large, we consider an atomic region ($r_1 \ll R$), therefore, the system is in fact deemed as a hydrogen-like atom perturbed by the charge Z_2: the unperturbed Hamiltonian is taken in the form:

$$H_0 = -\frac{\Delta_{r_1}}{2m} - \frac{Z_1}{r_1}, \tag{6}$$

and the perturbation H' is the Coulomb potential of the charge Z_2, and is expanded in powers of R^{-1}:

$$H' = -\frac{Z_2}{r_2} = -Z_2\sum_{n=1}^{\infty}\frac{r_1^n P_n(\cos\theta_1)}{R^{n+1}}. \tag{7}$$

Here θ_1 is the angle between the vectors $\mathbf{r}_1$ and $\mathbf{R}$.

Then for the unperturbed equation

$$H_0\psi_0(\mathbf{r}_1) = E_0\psi_0(\mathbf{r}_1). \tag{8}$$

The wave function for the $1s\sigma$ molecule-like state of $\mathrm{He}^+\bar{p}$ is asymmetric and may be written as

$$\psi_0(\mathbf{r}_1) = \frac{1}{\sqrt{\pi}}Z_1^{3/2}\,\mathrm{e}^{-Z_1 r_1}. \tag{9}$$

The wave function for the $1s\sigma_g$ electron state of H_2^+ molecular ion should be symmetrized and is written as

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\psi_0(\mathbf{r}_1) + \psi_0(\mathbf{r}_2)). \tag{10}$$

The ground state unperturbed energy is equal to

$$E_0 = -\frac{Z_1^2}{2}. \tag{11}$$

The perturbation (7) gives the first-order correction E_1 to the unperturbed energy, and neglecting the exponentially decreasing terms, one gets

$$E_1 = \langle\psi_0|H'|\psi_0\rangle \equiv \int d\mathbf{r}_1\psi_0^*(\mathbf{r}_1)H'\psi_0(\mathbf{r}_1) = -\frac{Z_2}{R}. \tag{12}$$

In order to obtain the first-order wave function, we consider the following one-electron and one-center equation with the perturbation in the dipole approximation $H' = -F_2 r_1\cos\theta_1$, a static field generated by the charge Z_2, and its contribution to the unperturbed energy is vanish due to a symmetry, and $F_2 = Z_2/R^2$ is electric field strength.

The wave equation for ψ_1 is

$$(E_0 - H_0)\psi_1 = H'\psi_0. \tag{13}$$

So that the first-order wave function for the $1s\sigma$ molecule-like state of $He^+\bar{p}$ is found

$$\psi_1(\mathbf{r}_1) = -\frac{F_2}{\sqrt{\pi}}Z_1^{3/2}\Big(\frac{r_1}{Z_1^2} + \frac{r_1^2}{2Z_1}\Big)\,\mathrm{e}^{-Z_1 r_1}\cos\theta_1, \tag{14}$$

where $Z_1 > Z_2$, and for the $1s\sigma_g$ electron state of H_2^+ molecular is taken in the form:

$$\psi_1(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}(\psi_1(\mathbf{r}_1) + \psi_1(\mathbf{r}_2)). \tag{15}$$

With the aid of the above wave functions, for the $1s\sigma_g$ electron state of H_2^+ molecular ion ($Z = Z_1 = Z_2$), one gets through the first-order approximation:

$$\langle V\rangle \equiv \langle\psi_0 + \psi_1|V|\psi_0 + \psi_1\rangle = -Z^2 - \frac{Z}{R} + \mathcal{O}(R^{-4}), \tag{16}$$

$$\big\langle V^2\big\rangle = 2Z^4 + \frac{2Z^3}{R} + \frac{Z^2}{R^2} + \mathcal{O}(R^{-4}), \tag{17}$$

$$\big\langle \mathbf{p}V^2\mathbf{p}\big\rangle = 2Z^6 + \frac{2Z^5}{R} + \frac{Z^4}{R^2} + \mathcal{O}(R^{-4}), \tag{18}$$

and for the $1s\sigma$ molecule-like state of antiprotonic helium $He^+\bar{p}$ ($Z_1 > Z_2$):

$$\langle V\rangle = -Z_1^2 - \frac{Z_2}{R} + \mathcal{O}(R^{-4}), \tag{19}$$

$$\big\langle V^2\big\rangle = 2Z_1^4 + \frac{2Z_1^2 Z_2}{R} + \frac{Z_2^2}{R^2} + \mathcal{O}(R^{-4}), \tag{20}$$

$$\big\langle \mathbf{p}V^2\mathbf{p}\big\rangle = 2Z_1^6 + \frac{2Z_1^4 Z_2}{R} + \frac{Z_1^2 Z_2^2}{R^2} + \mathcal{O}(R^{-4}). \tag{21}$$

In above asymptotic formulae (16)–(21), we neglect the exponentially decreasing terms.

2. RELATIVISTIC CORRECTIONS OF ORDER $m\alpha^6$ TO COULOMB TWO-CENTER PROBLEM

In this section we will think over the analytic calculation of relativistic corrections of order $m\alpha^6$ for the ground states of the system, but those had been described and calculated numerically in our previous letter [11].

Relativistic correction of order $m\alpha^6$ can be expressed as [11]

$$\Delta E^{(6)} = \left\langle H'_B Q (E_0 - H_0)^{-1} Q H'_B \right\rangle + \frac{3E_0 \left\langle V^2 \right\rangle}{4m^2} - \frac{5E_0^2 \left\langle V \right\rangle}{4m^2} - \frac{3\pi E_0 \left\langle (\rho_1 + \rho_2) \right\rangle}{4m^3} + \\ + \frac{\left\langle \mathbf{p} V^2 \mathbf{p} \right\rangle}{8m^3} + \frac{\left\langle V \right\rangle \left\langle H_B \right\rangle}{2m} + \frac{E_0^3}{2m^2}. \quad (22)$$

Here $Q = I - |\psi_0\rangle\langle\psi_0|$ is a projection operator and H_B is the Breit–Pauli Hamiltonian:

$$H_B = -\frac{\mathbf{p}^4}{8m^3} + \frac{1}{8m^2}[Z_1 4\pi\delta(\mathbf{r}_1) + Z_2 4\pi\delta(\mathbf{r}_2)] + \left(Z_1 \frac{[\mathbf{r}_1 \times \mathbf{p}]}{2m^2 r_1^3} + Z_2 \frac{[\mathbf{r}_2 \times \mathbf{p}]}{2m^2 r_2^3} \right) \mathbf{s}\,, \quad (23)$$

where $\mathbf{p}$ and $\mathbf{s}$ are the momentum and spin of an electron, respectively.

Then H'_B is the modified Breit–Pauli operator

$$H'_B = -\frac{p^4}{8m^3} + \frac{\pi}{m^2}[Z_1\delta(\mathbf{r}_1) + Z_2\delta(\mathbf{r}_2)] - \frac{1}{4m^2}(\boldsymbol{\mathcal{E}}_1 + \boldsymbol{\mathcal{E}}_2)\boldsymbol{\nabla} + 2U(H_0 - E_0), \quad (24)$$

where $U = -\dfrac{1}{4m}V$, $\boldsymbol{\mathcal{E}}_i = -Z_i \mathbf{r}_i / r_i^3$ and $\rho_i = Z_i \delta(\mathbf{r}_i)$ ($\Delta V = 4\pi\rho$).

To calculate the second-order contribution in Eq. (22) is a main task in this section. We firstly solve the following first-order approximation equation for the hydrogen-like atom, and use the solution ψ_1 to evaluate this second-order contribution for the system.

In the first-order approximation, the wave equation is

$$(E_0 - H_0)\psi_1 = (H_{\mathrm{BP}} - E_1)\psi_0, \quad (25)$$

where

$$H_{\mathrm{BP}} = -\frac{p^4}{8m^3} + \frac{Z_1\pi}{2m^2}\delta(\mathbf{r}_1), \quad E_1 = \langle H_{\mathrm{BP}} \rangle = -\frac{Z_1^4}{8}.$$

The solution of Eq. (25) ψ_1 is found in the form:

$$\psi_1 = \frac{Z_1}{4mr_1}\psi_0 + \tilde{\psi}_1, \quad (26)$$

where $\tilde{\psi}_1$ is a less singular function, $\tilde{\psi}_1 \sim \ln r_1$ at $r_1 \to 0$, and

$$\tilde{\psi}_1 = \Big(\frac{Z_1^2}{2} - \frac{Z_1^2}{2}\ln r_1 - \frac{Z_1^2}{2}\ln(2Z_1) - \frac{\gamma Z_1^2}{2} \Big)\psi_0,$$

where $\gamma \simeq 0.5772$.

Then without any difficulties in an integration, the second-order contribution is evaluated as

$$E_1^{(6)} = \left\langle H'_B Q (E_0 - H_0)^{-1} Q H'_B \right\rangle = \left\langle \tilde{\psi}_1 | (H'_{\rm BP} - \langle H_{\rm BP} \rangle) | \psi_0 \right\rangle . \tag{27}$$

In this evaluation, an explicit form of the modified Breit–Pauli operator is

$$H'_B = -\frac{p^4}{8m^3} + \frac{\pi}{m^2} Z_2 \delta(\mathbf{r}_2) + \frac{Z_1}{4m^2 r_1^2} \frac{\partial}{\partial r_1} + \frac{Z_2}{4m^2 r_2^2} \frac{\partial}{\partial r_2} + \frac{Z_1}{4m^2} \frac{\mathbf{r}_1 \mathbf{r}_2}{r_1^3 r_2} \frac{\partial}{\partial r_2} + \\ + \frac{Z_2}{4m^2} \frac{\mathbf{r}_1 \mathbf{r}_2}{r_1 r_2^3} \frac{\partial}{\partial r_1} + 2U(H_0 - E_0). \tag{28}$$

Substituting (28) into (27), and evaluating the integral, and neglecting the exponentially decreasing terms, we obtain the second-order contribution:

$$E_1^{(6)} = -\frac{Z_1^6}{4} + \mathcal{O}(R^{-4}). \tag{29}$$

The other terms except for the first term in Eq. (22) can be summed with the aid of the asymptotic formulae obtained in the previous section:

$$E_2^{(6)} = \frac{3E_0 \left\langle V^2 \right\rangle}{4m^2} - \frac{5E_0^2 \langle V \rangle}{4m^2} - \frac{3\pi E_0 \langle (\rho_1 + \rho_2) \rangle}{4m^3} + \frac{\left\langle \mathbf{p} V^2 \mathbf{p} \right\rangle}{8m^3} + \\ + \frac{\langle V \rangle \langle H_B \rangle}{2m} + \frac{E_0^3}{2m^2} = \frac{3Z_1^6}{16} + \mathcal{O}(R^{-4}). \tag{30}$$

In an evaluation of (30), we used

$$E_0 = -\frac{Z_1^2}{2} - \frac{Z_2}{R}, \quad p^4 = 4m^2 (E_0^2 - 2E_0 V + V^2). \tag{31}$$

Finally, the relativistic correction of order $m\alpha^6$ for the ground states of both hydrogen molecular ion H_2^+ and antiprotonic helium atom $He^+\bar{p}$ can be found analytically:

$$\Delta E^{(6)} = E_1^{(6)} + E_2^{(6)} = -\frac{Z_1^6}{4} + \frac{3Z_1^6}{16} = -\frac{Z_1^6}{16} + \mathcal{O}(R^{-4}). \tag{32}$$

In case of large R, the spin-orbit term of the Breit–Pauli Hamiltonian (23) gives us the result with the exponentially decreasing terms in frame of the second-order contribution, so that this calculation is omitted in this letter.

CONCLUSION

Asymptotic formulae of some expectation values related to the relativistic corrections in powers of R^{-1} for the $1s\sigma_g$ electron state of H_2^+ molecular ion and the $1s\sigma$ molecule-like state of antiprotonic helium $He^+\bar{p}$ have been derived through the first-order perturbation. Using asymptotic formulae the asymptotically analytic expression of evaluation of relativistic corrections of order $m\alpha^6$ for both ground states in reciprocal powers of R has been obtained up to accuracy of $\mathcal{O}(R^{-4})$, which had been presented and calculated numerically in [11].

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Appendix
ANALYTICAL EVALUATION AND DIVERGENT TERMS OF THE EXPECTATION VALUES

The calculation of the expectation values is reduced to evaluation of integrals of the type

$$\Gamma_{lm}(\alpha,\beta,R)=\int r_1^{l-1}r_2^{m-1}\,\mathrm{e}^{-\alpha r_1-\beta r_2}d^3\mathbf{r}. \tag{A.1}$$

Integers (l,m) are, in general, non-negative, but in case of singular matrix elements one of the indices can be negative.

The function Γ_{00} can be easily obtained:

$$\Gamma_{00}(\alpha,\beta,R)=\frac{4\pi}{R}\,\frac{\mathrm{e}^{-\beta R}-\mathrm{e}^{-\alpha R}}{\alpha^2-\beta^2}, \tag{A.2}$$

where R is the distance between nuclei, then $\Gamma_{lm}(\alpha,\beta,R)$ for non-negative (l,m) may be generated from (A.2) by means of relation

$$\Gamma_{lm}(\alpha,\beta,R)=\left(-\frac{\partial}{\partial\alpha}\right)^l\left(-\frac{\partial}{\partial\beta}\right)^m\Gamma_{00}(\alpha,\beta,R). \tag{A.3}$$

Integral $\Gamma_{-1,0}(\alpha,\beta,R)$ is expressed by

$$\Gamma_{-1,0}(\alpha,\beta,R)=\frac{2\pi}{R\beta}\Big\{\mathrm{e}^{-\beta R}[\ln R(\alpha+\beta)+\mathrm{Ei}\,(-(\alpha-\beta)R)]- \\ -\mathrm{e}^{-\beta R}\ln R(\alpha-\beta)-\mathrm{e}^{\beta R}\mathrm{Ei}(-(\alpha+\beta)R)\Big\}. \tag{A.4}$$

Worthy to note that a function in square brackets is analytic when argument is zero. Integrals $\Gamma_{-1,m}$ are generated from $\Gamma_{-1,0}$ similar to (A.3):

$$\Gamma_{-1,m}(\alpha,\beta,R)=\left(-\frac{\partial}{\partial\beta}\right)^m\Gamma_{-1,0}(\alpha,\beta,R). \tag{A.5}$$

The asymptotic series of exponential integral function encountered in (A.4) is [12]

$$\mathrm{Ei}\,(z)=\mathrm{e}^z\sum_{n=0}\frac{n!}{(z)^{n+1}},\quad -\mathrm{Ei}\,(-z)=\mathrm{e}^{-z}\sum_{n=0}(-)^n\frac{n!}{(z)^{n+1}}.$$

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