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Pair-function calculations for two-electron systems in model plasma environments

Zhengming Wang and Peter Winkler
Department of Physics, University of Nevada, Reno, Nevada 89557

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The pair-function formalism has been extended to the calculation of atomic and ionic properties in plasma environments that are modeled in terms of analytic screening potentials of the usual Debye form and the more general Debye-Laughton type. The theory has been applied to two-electron systems. As particular applications, the stability of H^- and the energy splitting of several $1sns$ and $1snp$ states of the He atom have been studied in model plasma environments as well as the energies of allowed and forbidden transitions.

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INTRODUCTION

The detailed study of atomic processes in plasma environments has become an active and relevant search topic in recent years. In such environments, the interaction between the core and the valence electrons with the atomic nucleus is screened. The potential between the nucleus and the electrons can be represented by different models, the most famous of which is the analytic exponential potential of Yukawa type. Several papers have discussed the energy levels of single-electron systems in this potential. Two relevant examples of such approaches are the fully numerical computation by Rogers, Grabosk, and Harwood [1] and a method of solving the Schrödinger equation with screened Coulomb potentials by Nauenberg [2], which makes ample use of recurrence relations. The calculation of autoionizing states turns out to be more difficult and requires the development of alternative techniques. Siegert boundary conditions have been successfully employed to solve such problems [3–5]. The complex coordinate dilatation method is an alternative tool [6–8]. The present authors extended Nauenberg's analytic treatment to encompass also resonances [9].

The physics background of these approaches is the approximation of the effects of the plasma charges on the interaction between the bound electrons and the atomic nuclei by a parametrized screening potential. It is interesting and feasible to study the behavior of a multielectron system with the interaction among the valence electrons taken into account explicitly while incorporating the effect of the plasma electrons and ion cores in the form of a screened background potential. This behavior becomes particularly relevant when ionizing and recombination processes in plasmas are involved. In the present work we study two-electron systems with a special focus on the stability of the ground state of H^- and He, as well as excited states of He in such environments with different degrees of screening. We are particularly interested in properties of these systems that can be used for plasma temperature and density diagnostics.

In principle, the standard methods of multielectron atomic calculations such as density function theory, multiconfiguration Hartree-Fock theory, or atomic many-body perturbation theory (MBPT) can be modified to include screening effects. This, however, has not yet been done.

This work is an attempt to extend MBPT to this field. The formalism of MBPT is used following the work by Morrison and co-workers [10–21] and the landmark calculation by Mårtensson of the ground states of the H^- ion and the He atom, as well as the $1s2s$ state of the He atom [13].

Section I of this paper deals with the potential. Section II introduces briefly both the relevant relations of MBPT and the numerical methods of solving the pair-function equations. Section III presents some results and discussion. A summary is presented in Sec. IV.

I. DEBYE-LAUGHTON POTENTIALS

Screened Coulomb potentials are widely used in simple models to approximate complicated many-body interactions, for instance, in the scattering of electrons from atoms, in plasmas, in liquid metals, and in electrolyte solutions. The most famous representative in the latter area is the Debye-Hückel theory.

This type of potential makes it not only feasible to involve the approximate interactions in the many-body system, but also satisfies the conditions of the resonance theory of Combes and co-workers [14,15] precisely. Therefore, various techniques, such as dilatation and exterior scaling methods, can be used.

In order to be prepared for a wide range of plasma conditions, one can study systems with the Debye-Laughton potentials. The analytic form of these potentials is given by

$$U(r)=-\frac{A}{r}\exp\left[-\frac{r}{D}\right]+B\exp\left[-\frac{(C+1)r}{D}\right]. \qquad (1)$$

By selecting the four parameters of A, B, C, and D, we can adjust the potentials to represent very different plasma environments. With a proper choice, the potential exhibits both a maximum and a minimum at finite values of r and can be adjusted to approximate other nonmonotonically screened potentials that have been proposed before, such as the exponential-cosine screened Coulomb potentials. With $C=0$, Laughton's modification adds a potential barrier to the Debye potential with its maximum at a distance of

$$r_{\max}=\frac{AD+\sqrt{A^2+4ABD}}{2B} . \tag{2}$$

II. PERTURBATION THEORY AND THE PAIR FUNCTION

The details of MBPT can be found in Refs. [10–12]. Here we only review briefly the main formulas for the case of two-electron systems.

We take the potential between the core and surrounding electrons as a Debye-Laughton potential, while the interaction between the electrons remains a pure Coulomb potential. The Hamiltonian of the two-electron system takes the form

$$H=H_0+\frac{1}{r_{12}} , \tag{3}$$

$$H_0=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2+U(r_1)+U(r_2) , \tag{4}$$

where U is the screening potential as discussed in Sec. I. The eigenvalues and eigenfunctions of H_0 are given as (e_a+e_b) and $|\{ab\}\rangle$. Here the curly brackets indicate the properly antisymmetrized wave function. The eigenfunctions of the Hamiltonian H can be written as

$$|\{\varphi_{ab}\}\rangle=|\{ab\}\rangle+\{\rho_{ab}\}\rangle . \tag{5}$$

Here $|\{\rho_{ab}\}\rangle$ is the pair function that represents the correlation part of the wave function that is not included in the product function $|\{ab\}\rangle$. Two-electron wave functions can be written in terms of nonsymmetric functions as

$$|\{\varphi_{ab}\}\rangle=\frac{1}{\sqrt{2}}|\varphi_{ab}(1,2)-\varphi_{ba}(1,2)\rangle , \tag{6}$$

$$|\{ab\}\rangle=\frac{1}{\sqrt{2}}|a(1)b(2)-a(2)b(1)\rangle , \tag{7}$$

and

$$|\{\rho_{ab}\}\rangle=\frac{1}{2}|\rho_{ab}(1,2)-\rho_{ba}(1,2)\rangle . \tag{8}$$

The pair function satisfies Bloch's equation

$$\begin{aligned}(\varepsilon_a+\varepsilon_b-H_0)|\rho_{ab}\rangle &=\sum_{rs\notin D}|rs\rangle\left\langle rs\left|\frac{1}{r_{12}}\right|ab+\rho_{ab}\right\rangle\\ &\quad-\sum_{cd\in D}|\rho_{cd}\rangle\left\langle cd\left|\frac{1}{r_{12}}\right|ab+\rho_{ab}\right\rangle . \end{aligned}\tag{9}$$

In solving the pair-function equation, it is convenient to separate the pair function into its radial, angular, and spin parts

$$\begin{aligned}\rho_{ab}=&\sum_{k,l_r,l_s}\frac{1}{r_1r_2}\rho(k,ab\rightarrow l_rl_s)\\ &\times\sum_{m_r,m_s}G(k,rsab)Y_{l_rm_r}(\theta_1\phi_1)\\ &\times Y_{l_sm_s}(\theta_2\phi_2)\sigma(1)\sigma(2) ,\end{aligned}\tag{10}$$

where G is an angular coupling factor as given in Ref. [13].

Then Eq. (9) yields a set of associated partial integro-differential equations that cannot be solved analytically. Two methods to compute approximate solutions have been proposed. Salomonson and Oster developed a finite discrete spectrum method to calculate the ground state of the He atom in 1989 [16], while Mårtensson [13] applied an iterative method of solution. In each iteration, only a partial differential equation is solved. The present work is based on the iterative approach. The main procedure has been described explicitly in Mårtensson paper. The approximate eigenvalue of H can be calculated by means of

$$\begin{aligned}E=\varepsilon_a+\varepsilon_b&+\left\langle\{ab\}\left|\frac{1}{r_{12}}\right|\{ab\}\right\rangle\\ &+\left\langle\{ab\}\left|\frac{1}{r_{12}}\right|\{\rho_{ab}\}\right\rangle .\end{aligned}\tag{11}$$

TABLE I. Ground-state energy of the negative hydrogen ion in Debye-Laughton potentials with $A=1$, $B=0$, $C=0$, and different D values. The asterisk indicates an unbound system. Energies are given in atomic units. D is given in atomic length units.

D	Ground-state energy of H^-	Ground-state energy of H
20	−0.434 03*	−0.451 82
32	−0.467 98*	−0.469 67
33.5	−0.470 34*	−0.470 85
34	−0.471 25	−0.471 23
35	−0.472 54	−0.472 05
50	−0.488 66	−0.480 29
100	−0.508 12	−0.490 07
200	−0.517 83	−0.495 02
1000	−0.525 70	−0.499 00
infinite	−0.527 32	−0.500 00

TABLE II. Ground-state energy of the negative hydrogen ion in Debye-Laughton potentials with $A=1$, $C=0$, and different B and D values. The asterisk indicates an unbound state. D is given in atomic length units.

$B\backslash D$	50	100	1000
0.002	−0.485 02	−0.504 11	−0.521 69
0.005	−0.479 34	−0.498 27	−0.515 70
0.010	−0.469 86	−0.488 57	−0.505 73
0.0138	−0.462 40*	−0.481 03	−0.498 11

All data in this paper are given in atomic units except when indicated otherwise. The calculations include contributions up to d symmetry (d limit).

III. RESULTS AND DISCUSSIONS

For plasma diagnostic purposes it is necessary to relate experimental quantities to relevant plasma parameters, such as particle density n_0 and temperature T. The radiation due to transitions between low-lying electronic states, i.e., those that are bound under not too extreme plasma conditions, as well as free-bound transitions are only two of various electron processes that are habitually utilized for diagnostics. For this purpose the knowledge of accurate transition energies as a function of the plasma parameters is mandatory. In this context the dependence of the Debye parameter D on the particle density and the temperature is used: D is proportional to $(T/n_0)^{1/2}$. The information on the transition energies (which is given in the present work) has to be augmented by an analysis of the typical line broadening in plasma environments (which has not been calculated here) as well as an investigation of the admixtures of optically forbidden lines that are common in plasmas due to the temporary breaking of the spherical symmetry. Under ideal circumstances the measurement of two transitions with different dependences on the parameter D would allow the determination of the two relevant quantities n_0 and T, always assuming the validity of the simple Debye model. In practice, such an analysis is based on a large variety of experimental information.

TABLE III. Relation between temperature T, the electron density n_e (in 10^{21} m^{-3}), the ratio N_H/n_{H^-} of the number densities of H and H$^-$, and the screening constant D, which is given in atomic length units. Each pair of values T and n_c has been determined so that the Saha-Boltzmann [17] equation and the defining equation for D are satisfied simultaneously.

n_H/n_{H^-}	0.1	0.2	0.5	1	2	5	10
				$D=35$			
T (K)	29	33	40	48	58	82	110
n_c	0.41	0.46	0.56	0.66	0.81	1.1	1.6
				$D=50$			
T (K)	360	400	460	520	590	720	860
n_e	2.5	2.7	3.1	3.5	4.0	4.9	5.8
				$D=100$			
T (K)	640	690	770	840	930	1080	1230
n_e	1.1	1.2	1.3	1.4	1.6	1.8	2.1

TABLE IV. Energies of $|1s2s\,^1S\rangle$ and $|1s2s\,^3S\rangle$ states, the energy splitting between these two states of the He atom in Debye-Laughton potentials with $A=2$, $B=0$, and $C=0$, and different D's. States with an asterisk are unbound. D is given in atomic length units.

D	$\|1s2s\,^1S\rangle$	$\|1s2s\,^3S\rangle$	Energy splitting	Eigenvalue of He$^+$(1s)
9	−1.754 590*	−1.785 696 *	0.021 106	−1.786 717
10	−1.796 123*	−1.820 088	0.023 965	−1.807 265
12	−1.847 463	−1.873 086	0.025 623	−1.838 404
20	−1.965 439	−1.991 352	0.026 913	−1.908 184
50	−2.066 355	−2.096 277	0.029 922	−1.960 298
100	−2.104 609	−2.134 688	0.030 079	−1.980 074
200	−2.124 305	−2.154 638	0.030 333	−1.990 182

In the modified form of the Debye-Laughton potential the parameter B has been introduced to add a potential barrier in order to be able to analytically represent potential shapes that are more in agreement with the results of *ab initio* Monte Carlo or molecular-dynamics approaches. By the same token, however, the familiar interpretation of screening in terms of the single parameter D and, in particular, its simple dependence on n_0 and T have been lost. Since the potential barrier is relevant only for dense plasmas that are controlled by collisions, as opposed to radiation, the few results that involve nonvanishing values of B (see Table II) are somewhat detached from the rest of the present data. A much more detailed analysis is required before they can be utilized for plasma diagnostics. To our knowledge this has not yet been done and lies well beyond the scope of the present work.

A. Stability of H$^-$

Tables I and II list the ground-states energies of H$^-$ in different screening potentials. From Table I, we see, as

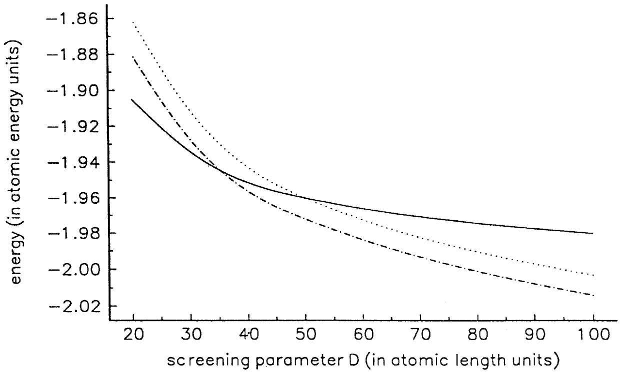

FIG. 1. Energy of the ground state of the He$^+$ ion (solid curve) compared to the energies of the $|1s3s\,^1S\rangle$ and $|1s3s\,^3S\rangle$ configurations of the He atom (dotted and dash-dotted curves, respectively) for different values of the screening parameter D of the unmodified Debye model.

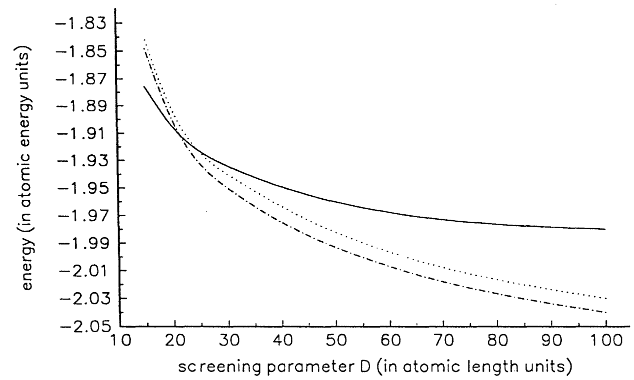

FIG. 2. Energy of the ground state of the He^+ ion (solid curve) compared to the energies of the $|1s4s\,{}^1S\rangle$ and the $|1s4s\,{}^3S\rangle$ configurations of the He atom (dotted and dash-dotted curves, respectively) for different values of the screening parameter D of the unmodified Debye model.

expected, that by increasing screening the system becomes less bound. Without screening (corresponding to infinite D) the energy is $-0.527\,32$ a.u., which is 0.027 32 a.u. lower than the ground-state energy of H. When D is about 34, the stability of H^- becomes critical, i.e., the system energy $-0.471\,25$ a.u. is very close to the ground-state energy of H at $-0.471\,43$ a.u. For D less than 34, H^- is unbounded. Assuming a ratio n_H/n_{H^-} of the density of neutral hydrogen atoms to negative hydrogen ions, one can, with the help of the Saha-Boltzman population analysis [17] and the usual definition of the Debye parameter D, associate a pair of temperature T and electron density n_e values with each value of the binding energy from Table I. This is shown in Table III.

B. 1*sns* states of the He atom

The 1*sns* electrons can exist in singlet states $|1sns\,{}^1S\rangle$ and triplet states $|1sns\,{}^3S\rangle$. The radial wave functions for the singlet state ${}^1S$ and the triplet state ${}^3S$ of the two-electron system are, respectively,

$$r_1r_2\psi^{s,t}(r_1,r_2)$$

$$=\frac{1}{\sqrt{2}}[P_{1s}(r_1)P_{ns}(r_2)\pm P_{ns}(r_1)P_{1s}(r_s)+\rho(1sns,r_1r_2)\pm\rho(ns1s,r_1r_2)]\ . \qquad (12)$$

The total interaction energy takes the form

$$\langle 1s,ns|V|1s,ns\rangle\pm\langle 1s,ns|V|ns,1s\rangle+\langle 1s,ns|V|\rho_{1sns}\rangle\pm\langle 1s,ns|V|\rho_{ns1s}\rangle\ , \qquad (13)$$

where + indicates spin singlet states while − stands for triplet states and we neglect higher-order contributions.

Table IV lists the final results of the energy of the $|1s2s\,{}^1S\rangle$ and $|1s2s\,{}^3S\rangle$ states of the He atom in a Debye-Laughton potential. The fourth column presents the splitting of the energy of the singlet and the triplet states. The energy splitting of the two configurations decreases with increased screening.

In Fig. 1 we show the energies of the ground states of the He^+ ion and the $|1s3s\rangle$ states of the He atom in different screened Coulomb potentials. The solid line represents the He^+ energy, while the dotted and the dash-dotted lines correspond to the energies of the $|1s3s\,{}^1S\rangle$ and the $|1s3s\,{}^3S\rangle$ states of He, respectively. When D decreases (i.e., the screening increases), the energies of both He^+ and the $|1s3s\,{}^1S\rangle$ and the $|1s3s\,{}^3S\rangle$ states of He increase, but at different rates. Figure 2 has the same meaning as Fig. 1, except that it refers to the energies of the $|1s4s\rangle$ states of the He atom.

C. Transition energies between the 1*s*2*p*, the 1*s*2*s*, and the ground state of the He atom

The 1*snp* electrons can exist in a singlet configuration $|1snp\,{}^1P\rangle$ or a triplet configuration $|1snp\,{}^3P\rangle$. The expressions for the wave functions and the energies of these configurations are similar to those discussed for the 1*sns* case. Columns 2, 4, and 5 in Table V show the energies of some transitions in the He atom under various screening conditions. The results listed in column 3 refer to a transition that is dipole forbidden in an isolated atom. In a plasma environment such transitions may occur and are in fact a valuable tool for plasma modeling and diagnostics. The transition energy increases between $|1s2p\,{}^1P\rangle$ and $|1s1s\,{}^1S\rangle$ states, as well as between $|1s2p\,{}^3P\rangle$ and $|1s1s\,{}^1S\rangle$ when the screening decreases, but decreases between $|1s2p\,{}^1P\rangle$ and $|1s2s\,{}^1S\rangle$ states. However, a similar trend has not been found for the transition energy between $|1s2p\,{}^3P\rangle$ and $|1s2s\,{}^3S\rangle$.

IV. SUMMARY

The pair-function approach has been used to calculate energies and wave functions of the two-electron system in

TABLE V. Transition energy between the ground states and some low excited states. $A=2$, $B=0$, and $C=0$. Data with an asterisk indicate unbound upper states.

D	$\lvert 1s2p\,{}^1P\rangle$-$\lvert 1s1s\,{}^1S\rangle$	$\lvert 1s2p\,{}^3P\rangle$-$\lvert 1s1s\,{}^1S\rangle$	$\lvert 1s2p\,{}^1P\rangle$-$\lvert 1s2s\,{}^1S\rangle$	$\lvert 1s2p\,{}^3P\rangle$-$\lvert 1s2s\,{}^3S\rangle$
10	0.764 29*	0.716 76*	0.042 24	0.028 68
20	0.784 88*	0.744 95*	0.037 93	0.026 24
50	0.793 12	0.751 96	0.037 36	0.027 27
100	0.793 16	0.762 05	0.037 23	0.026 18
200	0.793 29	0.762 12	0.037 21	0.026 34
infinite	0.793 49	0.762 34	0.037 20	0.026 29

Debye-Laughton potentials. When screening increases, the contribution of the interaction energy decreases for both the ground state of helium and excited 1*sns* states of He. He becomes also less bound. The critical value of D at which the two-electron system becomes unbound varies for different states. For higher excited states, this happened at larger values of D. The singlet configuration becomes unbound at a larger D than the triplet configuration. The transition energy can be used for plasma diagnostics.

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