Transition Energies and Emission Oscillator Strengths of Helium in Model Plasma Environments

X. Lopez, C. Sarasola, and J. M. Ugalde*

Kimika Fakultatea, Euskal Herriko Unibertsitatea, P.K. 1072, 20080 Donostia, Euskadi, Spain

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The transition energies and the oscillator strengths of both the ultraviolet and visible series of the helium atom have been calculated in a hot, weak coupling plasma environment, modeled in terms of the Yukawa potential. Our approach, based on the full configuration interaction method, is found to be superior to those based on the atomic many-body perturbation theory, for it converges smoothly to accurate vacuum values as the screening parameter approaches to zero and also behaves smoothly with respect to increasing screening. Thus, it could be useful for plasma diagnostic purposes.

1. Introduction

The significance of statically screened Coulomb potentials for many areas of physics has been highlighted in various earlier publications. There are many areas of physics for which the screened potentials are important, namely, the statistical thermodynamics of many-body systems in partially ionized gases, *i.e.*, plasmas,[1] nuclear and elementary particle physics,[2] atomic physics,[3] solid-state physics,[4] plasma physics,[5,6] and atomic collision physics.[7] The screened Coulomb potential can be represented by different models. In particular, for hot plasma environments, it has been demonstrated,[8] from a rigorous expansion of the partition function, that the effect of the plasma sea on localized two-particle interactions is to replace the Coulomb potential by an effective exponentially decaying potential (Yukawa potential), with a screening parameter, λ, proportional to $(n_0/T)^{1/2}$, n_0 being the plasma density and T its temperature. This is important because this dependence of the screening parameter with the plasma density and temperature, in combination with the transition energies between bound states, can be used for plasma diagnostic purposes.[5,9] Therefore, it turns out that obtaining accurate transition energies, as a function of the plasma's screening parameter, is of paramount importance. This motivated the present study on the energies and emission oscillator-strengths of dipole-allowed electronic transitions of the He atom in hot, weak coupling plasmas. In particular, our approach relies on the test-particle method,[10] which is extremely useful to calculate properties associated with the discrete nature of plasma particles. Thus, we will discuss the effect of the plasma sea on the ultraviolet principal series, $1^1S \leftarrow n^1P$ transitions, the visible principal series, $2^1S \leftarrow n^1P$ transition, the $2^3S \leftarrow n^3P$ transition energies, and the "dipole forbidden" $1^1S \leftarrow 2^3P$ transition energies. Nevertheless, it should be mentioned that other important properties of the spectrum of weakly coupled plasmas, like the line widths, are dominated by fluctuations[11] not accounted for in the test-particle method.

2. Methods

We adopt a full configuration interaction (FCI) approach to calculate all the various electronic states of interest of the Hamiltonian of our two-electron system

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z\left(\frac{e^{-\lambda_{en}r_1}}{r_1} + \frac{e^{-\lambda_{en}r_2}}{r_2}\right) + \frac{e^{-\lambda_{ee}r_{12}}}{r_{12}} \quad (1)$$

The details of FCI can be found elsewhere.[12] The wavefunction will contain all of the configuration-state functions (CSF's) that can be generated for our two-electron system, with all the atomic basis set functions. The latter have been expanded as linear combinations of Gaussian-like primitives, for which a complete analytical solution for all the required basic integrals is available.[13]

The range of the screening parameter λ, discussed in this paper, will be from 5×10^{-3} au to 0.1 au. For these values of λ, the plasma-coupling parameter is much smaller than unity, so that the statically shielded Hamiltonian of eq 1, is very reliable to describe the screened Coulomb interaction.[14−16] Also, it has been shown[17] that for such values of λ the expansion of the atomic orbitals in terms of a moderate set of Gaussian primitive functions leads to satisfactory results, compared with, in principle, more accurate Slater-type basis sets. One reason for this might be that since the Yukawa potential decays faster than the Coulomb potential, the Gaussian functions might fit this behavior better than exponential functions. Recall also that a recent calculation[5] has shown that at least both the 2^1S and the 2^3S excited states of the He atom exist for our selected values of the screening parameter.

Finally, it is worth mentioning that our method allows for direct comparison with vacuum calculations by setting $\lambda_{en} = \lambda_{ee} = 0$ in eq 1. Also, we have treated separately the screening effects on the electron−nucleus interaction and on the electron−electron interaction by using two screening parameters, λ_{en} for the former and λ_{ee} for the latter. This will enable comparison and assessment with respect to previous calculations.[5]

3. Results and Discussion

Firstly, the effect of the size of the basis set on the various excitation energies for the pure Coulombic ($\lambda_{en} = \lambda_{ee} = \lambda = 0$) interaction potential was studied. As expected, a large and flexible basis was found to be mandatory in order to obtain reliable results. Thus, Table 1 shows the behavior of various basis sets, of increasing quality, with respect to the $1^1S \leftarrow 2^1S$, $2^1S \leftarrow 3^1S$, $2^1S \leftarrow 2^1P$, $2^3S \leftarrow 3^3S$, and $2^3S \leftarrow 2^3P$ excitation energies. Inspection of Table 1 reveals that a well-balanced basis set, including s,p and d-type functions, is necessary for a reasonably accurate description of all the transitions studied. Notice that having a good set of s-type functions is crucial for the correct estimation of the $3^1S \leftarrow 2^1S$ and $3^3S \leftarrow 2^3S$ excitation energies, as observed by inspection of columns 3 and 5 of Table 1. We have found that the 6/5/5 basis set represents a very favorable balance of the computational cost with respect to the accuracy,

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TABLE 1: Excitation Energies, in au, for the Helium Atom in Vacuo, with Various Basis Sets[a]

basis sets	$2^1S \leftarrow 1^1S$	$2^1S \leftarrow 3^1S$	$2^1S \leftarrow 2^1P$	$2^3S \leftarrow 3^3S$	$2^3S \leftarrow 2^3P$
7/7/1	0.755 285	0.084 636	0.022 989	0.106 425	0.042 636
7/7/2	0.755 809	0.084 649	0.022 473	0.106 458	0.042 347
7/7/3	0.755 644	0.084 677	0.022 207	0.106 471	0.042 095
7/7/4	0.755 628	0.084 686	0.022 181	0.106 493	0.042 117
7/7/5	0.755 620	0.084 619	0.022 187	0.106 491	0.042 119
4/4/4	0.762 699	0.222 497	0.025 681	0.211 184	0.046 501
5/5/5	0.755 637	0.094 558	0.022 173	0.112 153	0.042 126
6/5/5	0.755 620	0.085 075	0.022 190	0.106 619	0.042 127
Exact	0.757 750[b]	0.084 702[b]	0.022 133[b]	0.106 540[b]	0.042 060[c]

[a] The basis sets are identified by their number of s-, p-, and d-type (first, second, and third numbers of the first column, respectively). The basis sets were constructed starting out from the standard 311*G*(3pd) basis,[24] 3/3/1 in our notation, and then complementary basis functions, with exponents 0.33 times that of the most diffuse one of each type, were added until the given size was reached. [b] Taken from ref 18 [c] Taken from ref 19.

TABLE 2: Energies for $\lambda = 0$ (in au) of $|1s2s^1S>$ and $|1s2s^3S>$ States of He[a]

λ	$\|1s2s^1S>$	$\|1s2s^3S>$	energy splitting
0.005	−2.124 719	−2.154 046	−0.029 327
	(−2.124 305)	(−2.154 638)	(0.030 333)
0.01	−2.105 157	−2.134 424	−0.029 266
	(−2.104 609)	(−2.134 668)	(−0.030 079)
0.02	−2.066 875	−2.095 9051	−0.029 030
	(−2.066 355)	(−2.096 277)	(−0.029 922)
0.05	−1.958 400	−1.985 899	−0.027 499
	(−1.965 439)	(−1.991 352)	(−0.025 913)
0.1	−1.797 310	−1.819 737	−0.022 427
	(−1.796 123)	(−1.820 088)	(−0.023 965)

[a] Values in parentheses, which correspond to the MBPT calculation, are taken from ref 5.

as compared to the "exact" values reported in the literature.[18,19] Hence, hereafter, all calculations will be carried out with the 6/5/5 basis set.

A. Energy Splitting between 2^1S and 2^3S States. We compare in Table 2 our final results for the $|1s2s^1S>$ and $|1s2s^3S>$ states of the He atom, with earlier calculated values using the many-body perturbation theory (MBPT) of Morrison et al.[20] modified to include screening effects.[5] Recall that we have set $\lambda_{ee} = 0$ in the electron−electron repulsion term of eq 1 to allow for comparison with the above data. The overall trend of the two data sets of Table 2 is that the energy of both $|1s2s^1S>$ and $|1s2s^3S>$ configurations decreases as the screening parameter increases. Also, the energy splitting between these electronic states decreases with increasing screening. However, while this trend is nicely observed by our results, those of Wang and Winkler[5] do not follow the above-mentioned pattern at the largest value of the screening parameter, for which, incidentally, the largest energy splitting is obtained. Also, we would like to mention that for all values of λ, our energy splitting is smaller than that of Wang and Winkler, except for $\lambda = 0.05$, for which we predict an energy splitting 0.001 586 au larger. Indeed, as shown in Figure 1, our results do behave smoothly with respect to λ, but Wang and Winkler's do not. Hence, we believe that our method is more stable than theirs with respect to increasing screening and, therefore, more reliable to predict accurately also the transition energies between various electronic states of interest. This will be shown in the forthcoming section.

B. Transition Energies and Oscillator Strengths. The ultraviolet principal series of the He atom consists of the electronic transitions between the 1^1S state and the singlet $|1snp,^1P>$ excited states. We have calculated both the transition energy and the emission oscillator strength associated with the lowest energy transition of the series, namely the $|1s^2,^1S> \leftarrow |1s2p,^1P>$ transition, as a function of the screening parameter, and compared with experiment for $\lambda_{ee} = \lambda_{en} = 0$ and with previous theoretical calculations for various values of λ. Results are collected in Table 3 for discussion. Notice that both our and Wang and Winklers' transition energies[5] show the same smoothly decreasing behavior. However, notice also that they predict larger transition energies, though it is interesting to point out that for the Coulombic potential case, $\lambda_{ee} = \lambda_{en} = 0$, Wang and Winkler overestimate the experimental transition energy[21] of 0.779 748 au by 1.37×10^{-2} au, while we underestimate it by 1 less order of magnitude, namely, 1.94×10^{-3} au. This and the smoother behavior shown in the previous section suggest that our calculations might be more accurate than earlier ones for the entire range of the screening parameter.

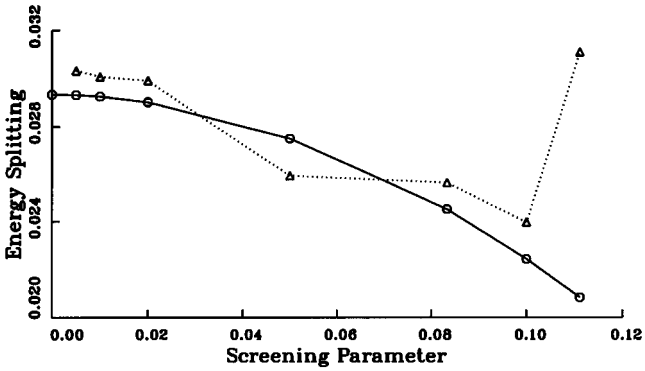

Figure 1. Energy splitting, in atomic units, of the 2^1S and 2^3S electronic states of the helium atom, as a function of the screening parameter. Present work: solid curve. Reference 5: dotted curve.

TABLE 3: Transition Energies in au, with $\lambda_{ee} = 0$ and $\lambda_{en} = \lambda$, $E^0{}_{1^1S\leftarrow 2^1P}$, and with $\lambda_{ee} = \lambda_{en} = \lambda$, $E^1{}_{1^1S\leftarrow 2^1P}$, and Their Corresponding Oscillator Strengths, f, for Different Values of the Screening Parameter[a]

λ	$E^0{}_{1^1S\leftarrow 2^1P}$	$f^0{}_{1^1S\leftarrow 2^1P}$	$E^1{}_{1^1S\leftarrow 2^1P}$	$f^1{}_{1^1S\leftarrow 2^1P}$
0.005	0.777 711	0.091 603	0.777 758	0.091 652
	(0.793 29)			
0.01	0.777 420	0.091 306	0.777 603	0.091 504
	(0.793 16)			
0.02	0.776 285	0.090 166	0.777 000	0.090 934
	(0.793 12)			
0.05	0.768 739	0.082 926	0.773 027	0.087 353
	(0.784 88)			
0.1	0.743 475	0.061 649	0.760 145	0.076 817
	(−)			

[a] Values in parentheses are taken from ref 5.

Including screening of the electron−electron Coulombic interaction increases slightly the value of the transition energy (see column 4 in Table 3), and maintains the smoothly decreasing behavior of the transition energy with the screening parameter.

The calculated emission oscillator strengths also decrease with increasing λ, for both cases $\lambda_{ee} = 0$, $\lambda_{en} = \lambda$, and $\lambda_{ee} = \lambda_{en} = \lambda$, as shown in columns 3 and 5 of Table 3. However, it is observed that the predicted values for $f^1{}_{1^1S\leftarrow 2^1P}$ are invariably larger than their corresponding $f^0{}_{1^1S\leftarrow 2^1P}$ values, with appreciably differences for the largest λ values investigated.

The lowest energy electronic transition of the visible singlet principal series, $|1s2s^1S> \leftarrow |1s2p^1P>$, was studied next. The experimental value[21] for this transition energy in vacuum is 0.022 132 au. Our method comes up with a value of 0.022 190 au, much better than that of Wang and Winkler,[5] 0.03720 au. As shown in Table 4, both the transition energy and the oscillator strength increases smoothly when the screening increases, irrespective of whether both the electron−electron and the

TABLE 4: Transition Energies in au, with $\lambda_{ee} = 0$ and $\lambda_{en} = \lambda$, $E^0{}_{2^1S\leftarrow 2^1P}$, and with $\lambda_{ee} = \lambda_{en} = \lambda$, $E^1{}_{2^1S\leftarrow 2^1P}$, and the Corresponding Oscillator Strengths, *f*, for Different Values of the Screening Parameter[a]

λ	$E^0{}_{2^1S\leftarrow 2^1P}$	$f^0{}_{2^1S\leftarrow 2^1P}$	$E^1{}_{2^1S\leftarrow 2^1P}$	$f^1{}_{2^1S\leftarrow 2^1P}$
0.005	0.022 193	0.126 523	0.022 192	0.126 455
	(0.037 21)			
0.01	0.022 201	0.126 924	0.022 195	0.126 657
	(0.037 23)			
0.02	0.022 230	0.128 481	0.022 210	0.127 433
	(0.037 36)			
0.05	0.022 388	0.138 859	0.022 294	0.132 422
	(0.037 93)			
0.1	0.022 699	0.177 762	0.022 475	0.148 369
	(0.042 24)			

[a] Values in parentheses are taken from ref 5.

TABLE 5: Transition Energies in au, with $\lambda_{ee} = 0$ and $\lambda_{en} = \lambda$, $E^0{}_{2^3S\leftarrow 2^3P}$, and with $\lambda_{ee} = \lambda_{en} = \lambda$, $E^1{}_{2^3S\leftarrow 2^3P}$, and the Corresponding Oscillator Strengths, *f*, for Different Values of the Screening Parameter[a]

λ	$E^0{}_{2^3S\leftarrow 2^3P}$	$f^0{}_{2^3S\leftarrow 2^3P}$	$E^1{}_{2^3S\leftarrow 2^3P}$	$f^1{}_{2^3S\leftarrow 2^3P}$
0.005	0.042 121	0.180 302	0.042 124	0.180 250
	(0.026 34)			
0.01	0.042 102	0.180 620	0.042 115	0.180 415
	(0.026 18)			
0.02	0.042 027	0.181 856	0.042 079	0.181 053
	(0.027 27)			
0.05	0.041 494	0.190 036	0.041 841	0.185 164
	(0.026 24)			
0.1	0.039 173	0.219 065	0.040 975	0.198 203
	(0.028 68)			

[a] Values in parentheses are taken from ref 5.

electron−nucleus or only the electron−nucleus type of interactions are screened. This suggests that the screening is more effective for the 2^1P than for the 2^1S state.

The lowest energy electronic transition of the visible triplet principal series, $2^3S\leftarrow 2^3P$, has also been studied in the present work and in that of Wang and Winkler.[5] The latter authors found a nonmonotonic behavior for the transition energy and reported a value of 0.02629 au for the transition in vacuum. This figure must be compared with the value of 0.04206 au given by the Accad *et al.*[19] and our prediction of 0.042 127 au. Contrary to previous calculations,[5] we predict a smoothly decreasing monotonic behavior of the $2^3S\leftarrow 2^3P$ transition energy, irrespective of whether screening effects are allowed for both the electron−electron repulsion and the electron−nucleus attraction or only for the latter, as shown in Table 5. Also, we found that the oscillator strength associated with this transition increases with increasing screening.

Finally, we would like to comment on the dipole-forbidden $1^1S\leftarrow 2^3P$ transition. The importance of such forbidden lines has been illustrated magnificently by Garstang,[22] and recently, the role and interest of such a transitions in astrophysical and laboratory plasma studies has been renewed.[23] In particular, the $1^1S\leftarrow 2^3P$ experimental transition energy in vacuum[21] is 0.770 417 au, which is to be compared with the earlier reported[5] energy of 0.76234 au and our predicted value of 0.768 399 au. Clearly, as well as for the all other transition energies, our method leads to more accurate values. Table 6 presents the transition energies as a function of λ for both screened electron−electron and electron−nucleus interactions, $E^1{}_{1^1S\leftarrow 2^3P}$, and screened electron−nucleus, unscreened electron−electron interactions, $E^0{}_{1^1S\leftarrow 2^3P}$. The latter values allow for direct comparison with those of Wang and Winkler.[5] Inspection of Table 6 reveals that the $1^1S\leftarrow 2^3P$ transition energy decreases as λ increases. However, it is worth noting that when both electron−electron and electron−nucleus interactions are screened, sligthly larger transition energies are obtained. Also, notice that our method predicts a slower decrease of the transition energy as a function of λ than the modified MBPT of Wang and Winkler.[5]

TABLE 6: Transition Energies in au, with $\lambda_{ee} = 0$ and $\lambda_{en} = \lambda$, $E^0{}_{1^1S\leftarrow 2^3P}$, and with $\lambda_{ee} = \lambda_{en} = \lambda$, $E^1{}_{1^1S\leftarrow 2^3P}$[a]

λ	$E^0{}_{1^1S\leftarrow 2^3P}$	$E^1{}_{1^1S\leftarrow 2^3P}$
0.005	0.768 312	0.768 353
	(0.762 12)	
0.01	0.768 055	0.768 217
	(0.762 05)	
0.02	0.767 052	0.767 685
	(0.751 90)	
0.05	0.760 346	0.764 160
	(0.744 95)	
0.1	0.737 522	0.752 593
	(0.716 76)	

[a] Values in parentheses are taken from ref 5.

4. Summary

We have investigated the first lines in both the ultraviolet and the visible series of the emission spectrum of the helium atom, in its singlet and triplet spin states, as well as the "dipole forbidden" $2^3P\leftarrow 1^1S$ transition, in the Yukawa potential. This model has been found to be accurate enough to describe hot, weak coupling plasma environments, through the screening paramenter λ, of the exponential of the potential. Our approach to the solution of the screened Hamiltonian is based on the full configuration interaction method, with carefully selected Gaussian-type basis sets. The availability of analytical formulas for the required molecular integrals makes this method very convenient from a computational viewpoint. In addition, we have shown that it is very stable and that it behaves smoothly with respect to the increase of the screening parameter. In particular, we have found that our method is more reliable than those based on the atomic many-body perturbation theory (MBPT). Thus, unlike the MBPT results, our calculations show a monotonic behavior of both the transition energies and their associated oscillator strengths for all the electronic transitions studied. In general, it is observed that the $|1s^2,{}^1S> \leftarrow |1s2p,{}^1P>$ and the $|1s2s,{}^3S> \leftarrow |1s2p^3P>$ parameters decrease as the screening parameter increases, while for the $|1s2s,{}^1S> \leftarrow |1s2p,{}^1P>$ transition both the transition energy and its oscillator strength increase with increasing screening. Finally, it should be pointed out that the energy of the $|1s^2,{}^1S> \leftarrow |1s2p,{}^3P>$ "dipole-forbidden" transition decreases as the screening increases. Recall that since the screening parameter is proportional to the square root of the density temperature ratio of the plasma, the transition energies can be useful for plasma diagnostic purposes.

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