Critical screening in the one- and two-electron Yukawa atoms

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The one- and two-electron Yukawa atoms, also referred to as the Debye-Hückel or screened Coulomb atoms, have been topics of considerable interest both for intrinsic reasons and because of their relevance to terrestrial and astrophysical plasmas. At sufficiently high screening the one-electron Yukawa atom ceases to be bound. Some calculations appeared to suggest that as the screening increases in the ground state of the two-electron Yukawa atom (in which both the one-particle attraction and the interparticle repulsion are screened) the two electrons are detached simultaneously, at the same screening constant at which the one-electron atom becomes unbound. Our results rule this scenario out, offering an alternative that is not less interesting. In particular, it is found that for $Z < 1$ a mild amount of screening actually increases the binding energy of the second electron. At the nuclear charge $Z_c \approx 0.911028\ldots$, at which the bare Coulomb two-electron atom becomes unbound, and even over a range of lower nuclear charges, an appropriate amount of screening gives rise to a bound two-electron system.

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I. INTRODUCTION

In the present paper we consider the behaviors of the nonrelativistic one- and two-electron Yukawa atoms, in which both the one-particle attractive and the interparticle repulsive Coulomb interactions are multiplied by exponentially decaying screening factors. Such potentials are also referred to as the Debye-Hückel [1] or screened Coulomb potentials. Thus, the screened hydrogenlike atom is specified by the Hamiltonian

$$\mathfrak{h}_{\rm Yu} = -\frac{1}{2}\nabla^2 - \frac{Z\exp(-\lambda r)}{r}, \tag{1}$$

and the screened heliumlike atom is specified by

$$\mathcal{H}_{\rm Yu} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - Z\left(\frac{\exp(-\lambda r_1)}{r_1} + \frac{\exp(-\lambda r_2)}{r_2}\right) + \frac{\exp(-\lambda r_{12})}{r_{12}}. \tag{2}$$

The extensive work done on the one-electron case is reviewed in Sec. II. In particular, the value of λ at which the ground state ceases to be bound and its (trivial) Z dependence have been determined (by several authors). There is little that we can add on this matter. In the two-electron case we seek the value of λ at which the binding energy of the second electron vanishes. Although this issue was also studied by several authors, whose work is reviewed in Sec. III, it turns out that some interesting features have not been properly dealt with. The claim that motivated our curiosity is that in the ground state of the two-electron Yukawa atom, upon raising the nonlinear screening constant, the two electrons simultaneously cease being bound, at the same critical screening constant at which the one-electron Yukawa atom becomes unbound [2–5]. This is sharply different from the He-isoelectronic sequence, where the critical charge below which only one electron remains bound is $Z_c \approx 0.91102822407725573$ [6], but this remaining electron remains bound for all $Z > 0$. Hence, one would wish to understand how the transition from the unscreened to the screened behavior takes place. The two electrons would trivially unbind simultaneously if no interelectronic repulsion existed. They could unbind simultaneously if the expectation value of the interelectronic repulsion vanished more rapidly than the one-electron components of the energy, upon approaching the critical charge. In any case, a more careful examination of this issue appears worthwhile, and the results reported below, that refute the claim cited above and extrapolate in an interesting manner to the bare Coulomb scenario, clearly justify this effort.

A rigorous study of the behavior of the spectra of short-range one-particle systems bound by potentials that depend linearly on the real parameter μ, i.e.,

$$\mathfrak{h} = -\tfrac{1}{2}\nabla^2 + \mu V,$$

was presented by Klaus and Simon [7]. Upon lowering the parameter μ, a threshold, $\mu^{(c)}$, is often observed at which an eigenvalue vanishes. In three dimensions the approach to this

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threshold can take place in one of two ways:

$$\text{Case A:} \quad E(\mu) \approx \alpha(\mu - \mu^{(c)})^2,$$

or

$$\text{Case B:} \quad E(\mu) \approx \alpha(\mu - \mu^{(c)}).$$

In case A the wave function becomes infinitely diffuse ("expands") upon approaching $\mu^{(c)}$. In case B $\lim_{\mu\to\mu^{(c)}} E(\mu)$ remains an eigenvalue, i.e., the corresponding wave function remains bound (square integrable). Klaus and Simon further show that if the potential V is spherically symmetric then the s-type eigenfunctions correspond to case A, and the $\ell \geqslant 1$ eigenfunctions correspond to case B. The applicability of the Klaus-Simon results to the one-electron Yukawa atom is not obvious, since the dependence of the potential on the screening parameter λ is nonlinear. However, it will be made more plausible in Sec. II.

For two identical particles described by the Hamiltonian

$$\mathcal{H} = -\tfrac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \mu_1[V(r_1) + V(r_2)] + \mu_2 W(r_{12}), \tag{3}$$

the existence of one- and two-particle bound states was investigated by Pont and Serra [8] over the whole upper right parameter quadrant ($\mu_1 > 0, \mu_2 \geqslant 0$). The existence of ground-state domains in which no particle, one particle, or two particles are bound implies the existence of appropriate boundaries within the (μ_1,μ_2) quadrant. However, the realization that a boundary separating the zero- and two-particle domains (a "2-0 line") is feasible strikes us as counterintuitive, hence remarkable. Crossing such a boundary in the appropriate direction, the two-electron system loses both electrons simultaneously. In addition to some "technical" demands concerning the potentials $V(r_i)$, $i = 1,2$, and $W(r_{12})$, it is required that both $V(r)$ and $W(r)$ decay at infinity, $W(r)$ be everywhere repulsive, and $-V(r)$ be attractive enough to give rise to a one-particle bound state for all $\mu_1 > \mu_1^{(c)} > 0$. Three types of behavior were identified for short-range one-particle potentials: case 1, no 2-0 line; case 2, finite 2-0 line; case 3, infinite 2-0 line. One- and two-particle critical exponents were defined, specifying the dependence of the binding energy on $\mu^{(c)} - \mu$ near the corresponding critical points. The values of these critical exponents were shown to identify the different types of behavior in a manner that resembles the Klaus-Simon [7] results referred to above. Remarkably, for one-body attractive Coulomb potentials all three types of behavior are feasible, depending on the form of the two-particle repulsion. Some further results established in [8], that are pertinent to the issue we are concerned with, are the following.

(1) For all $\mu_1 > \mu_1^{(c)}$ there is some $\mu_2^* > 0$ such that if $0 \leqslant \mu_2 \leqslant \mu_2^*$ then the Hamiltonian, Eq. (3), supports at least one bound state.

(2) Consider the case in which the one-particle wave function spreads (becomes infinitely diffuse, case A) when $\mu_1 \to \mu_1^{(c)}$ from above. Turning μ_2 on while μ_1 is just slightly higher than $\mu_1^{(c)}$, if $W(r_{12})$ is short range enough then the particles are sufficiently far apart that they do not repel one another appreciably, and a bound state can exist for some range of $\mu_2 > 0$. This cannot happen when $W(r_{12})$ is long range enough to tear apart the system for all $\mu_2 > 0$, near $\mu_1 \sim \mu_1^{(c)}$.

(3) Competition between a long-range attractive one-particle potential and a short-range interparticle repulsion can give rise to a *rebinding* phenomenon for some two-body systems, when the attractive coupling is decreased. The authors of [8] view this very remarkable observation as the main result of their work.

Yet another recent contribution that provides worthwhile insight, that is relevant to our present concern, deals with the existence of Borromean binding in three-particle systems with screened Coulomb interactions [9]. The existence of (rather narrow) ranges of the screening parameter was established, at which the three-particle system is bound whereas no two-particle subsystem is.

II. THE ONE-ELECTRON YUKAWA ATOM

A. Review of earlier results

The potential in the one-electron Hamiltonian, Eq. (1), appears to depend on the two parameters Z and λ, on the first one linearly and on the second one nonlinearly. However, scaling the coordinates via $\tilde{\vec{r}} = Z\vec{r}$ we obtain

$$\mathfrak{h}_{\rm Yu} = Z^2\left[-\frac{1}{2}\tilde{\nabla}^2 - \frac{1}{\tilde{r}}\exp\left(-\frac{\lambda}{Z}\tilde{r}\right)\right], \tag{4}$$

i.e., the one-electron ground state satisfies [10–12]

$$E_1(Z,\lambda) = Z^2 E_1\left(1, \frac{\lambda}{Z}\right). \tag{5}$$

It follows that the critical screening constant, at which the ground-state energy vanishes, satisfies

$$\frac{\lambda^{(c)}(Z)}{Z} = \lambda^{(c)}(1),$$

that we shall usually write as $\lambda^{(c)}$, or, later on, as $\lambda_1^{(c)}$, to indicate that it refers to the one-electron atom.

Several authors, using a variety of techniques, studied the ground-state critical screening constant for the Yukawa one-electron atom. Kesarwani and Varshni [13] recorded, in 1978, nine different calculations, only three of which provided five (or more) digit accuracy, i.e., $\lambda^{(c)} \approx 1.1906$. The earliest such computation, cited in [13], is due to Hulthén and Laurikainen [14]. The same value can be evaluated from the energies presented by Vrscay [15]. Diaz *et al.* [16] claimed 16 digit accuracy but their value disagrees in the eighth decimal place with the value proposed by Gomes *et al.* [17], $\lambda^{(c)} \approx 1.19061227 \pm 0.00000004$. Roy [18] obtained $\lambda^{(c)} \approx 1.190610$.

The dependence of Vrscay's energies [15] on $(\lambda^{(c)} - \lambda)$ near the critical screening parameter, for the ground as well as for the $2s$ state, is quadratic (case A), whereas for the $2p$ state it is linear (case B). These asymptotic properties are consistent with the Klaus-Simon theorem [7].

B. The one-electron computational procedure

One-electron ground-state energies and wave functions were calculated using a high-precision MAPLE implementation of Guimarães and Prudente's polynomial finite element method [19]. As a test of the accuracy of this computation, a variational function consisting of a 25-term expansion in powers of r,

multiplied by a crudely optimized exponential, was used to evaluate the ground-state energy at $Z = 0.68$, $\lambda = 0.6643$, a point of some special significance to be discussed below. The energy obtained using the Guimarães and Prudente procedure is -0.0060009755. The alternative procedure yields the same value, to all digits presented. The expectation value $\langle \exp(-\lambda r)\rangle$ is 0.123613702 versus 0.123613700, and the expectation value $\langle \frac{\exp(-\lambda r)}{r}\rangle$ is 0.099766511 versus 0.099766509, respectively.

C. The one-electron virial and Hellmann-Feynman theorems

Let $\Psi(r)$ be the normalized ground-state eigenfunction. Define $\tilde{\Psi}(r) = \eta^{\frac{3}{2}}\Psi(\eta r)$. Clearly, $\tilde{\Psi}(r)$ remains normalized. The expectation value of the one-electron Hamiltonian, Eq. (1), with respect to $\tilde{\Psi}(r)$ is

$$\tilde{E}_1 = \eta^2 T_1 - Z\langle\tilde{\Psi}(r)|\frac{\exp(-\lambda r)}{r}|\tilde{\Psi}(r)\rangle,$$

where $T_1 = \langle\Psi(r)| - \frac{1}{2}\nabla^2|\Psi(r)\rangle$. Since $\tilde{E}_1$ obtains its minimum at $\eta = 1$ [where $\tilde{\Psi}(r)$ is the ground-state eigenfunction], writing $\frac{\partial\tilde{E}_1}{\partial\eta}|_{\eta=1} = 0$ we obtain the virial theorem

$$2T_1 + V_1 = 2E_1 - V_1 = \lambda Z\langle\exp(-\lambda r)\rangle, \tag{6}$$

where $E_1 = T_1 + V_1$, and, using the notation $\langle\hat{O}\rangle \equiv \langle\Psi|\hat{O}|\Psi\rangle$, $V_1 = -Z\langle\frac{\exp(-\lambda r)}{r}\rangle$.

The Hellmann-Feynman theorem with respect to Z (which we shall refer to as the Z-Hellmann-Feynman theorem) yields

$$Z\frac{\partial E_1}{\partial Z} = -Z\left\langle\frac{\exp(-\lambda r)}{r}\right\rangle = V_1. \tag{7}$$

The λ-Hellmann-Feynman theorem yields

$$\frac{\partial E_1}{\partial\lambda} = Z\langle\exp(-\lambda r)\rangle. \tag{8}$$

Using Eq. (6) we obtain

$$\lambda\frac{\partial E_1}{\partial\lambda} = 2T_1 + V_1 = 2E_1 - V_1,$$

or

$$V_1 = 2E_1 - \lambda\frac{\partial E_1}{\partial\lambda} \tag{9}$$

and

$$T_1 = -E_1 + \lambda\frac{\partial E_1}{\partial\lambda}. \tag{10}$$

Substituting in Eq. (7) we finally obtain

$$Z\frac{\partial E_1}{\partial Z} + \lambda\frac{\partial E_1}{\partial\lambda} = 2E_1,$$

which is consistent with Eq. (5).

A numerical examination of the virial-Hellmann-Feynman relations allows an assessment of the accuracy of the computed results. Evaluating $E_1(Z,\lambda = 1)$ at $Z = 0.996, 0.998, 1.000, 1.002, 1.004$ we obtain the five-point estimate $\frac{\partial E_1}{\partial Z}|_{Z=1,\lambda=1} = -0.13018680$. In a similar way we obtain $\frac{\partial E_1}{\partial\lambda}|_{Z=1,\lambda=1} = 0.10961522$. Hence, we obtain $Z\frac{\partial E_1}{\partial Z}|_{Z=1,\lambda=1} + \lambda\frac{\partial E_1}{\partial\lambda}|_{Z=1,\lambda=1} = -0.02057158$, which agrees, to all decimals presented, with $2E_1$.

Upon approaching the critical screening constant from below, if E_1 vanishes quadratically in $(\lambda^{(c)} - \lambda)$, then T_1 and V_1 vanish as well, whereas they do not if E_1 vanishes linearly. However, in both cases

$$\lim_{\lambda\to\lambda^{(c)}} -\frac{V_1}{T_1} = 1. \tag{11}$$

Definition 1. We say that a wave function becomes infinitely diffuse ("expands") at $\lambda^{(c)}$, if, for all $R > 0$ and (arbitrarily small) $\epsilon > 0$, there is some $\delta > 0$ such that for $0 < (\lambda^{(c)} - \lambda) < \delta$ the inequality $\int_0^R |\Psi|^2 4\pi r^2 dr < \epsilon$ is satisfied.

Lemma 1. At the critical screening constant, at which $E_1(\lambda)$ vanishes, the wave function becomes infinitely diffuse if and only if $\lim_{\lambda\to\lambda^{(c)}}\frac{\partial E_1}{\partial\lambda} = 0$.

Proof. While $\langle\Psi|\Psi\rangle = 1$ for all $\lambda < \lambda^{(c)}$, if the wave function becomes infinitely diffuse at $\lambda^{(c)}$ then

$$\lim_{\lambda\to\lambda^{(c)}}\langle\Psi|\exp(-\lambda r)|\Psi\rangle = 0, \tag{12}$$

yielding, by Eq. (6), $\lim_{\lambda\to\lambda^{(c)}} V_1 = 0$; hence, by Eq. (7), $\lim_{\lambda\to\lambda^{(c)}}\frac{\partial E_1}{\partial\lambda} = 0$. On the other hand, if $\lim_{\lambda\to\lambda^{(c)}}\frac{\partial E_1}{\partial\lambda} = 0$, then Eq. (7) yields $\lim_{\lambda\to\lambda^{(c)}} V_1 = 0$, and, with Eq. (6), $\lim_{\lambda\to\lambda^{(c)}}\langle\exp(-\lambda r)\rangle = 0$, which can only happen if $\Psi(\vec{r})$ becomes infinitely diffuse, since $\exp(-\lambda r)$ is everywhere positive. ■

Remark 1. Case A states $E_1 \approx \alpha(\lambda^{(c)} - \lambda)^2$, hence $\frac{\partial E_1}{\partial\lambda}|_{Z_c} = 0$. Since the latter is (by the Hellmann-Feynman theorem, discussed above) the expectation value of an everywhere negative operator, the wave function must become infinitely diffuse at the critical charge, in agreement with the Klaus-Simon theorem [7]. Case B states $E_1 \approx \alpha(\lambda^{(c)} - \lambda)$, hence $\frac{\partial E_1}{\partial\lambda}|_{Z_c} = \alpha \neq 0$, implying that $\lim_{\lambda\to\lambda^{(c)}} V_1 \neq 0$, which is only possible if the wave function remains bound at $\lambda^{(c)}$. Hence, Lemma 1 fully agrees with the Klaus-Simon theorem, although the Hamiltonian is nonlinear in λ.

On the other hand, from the relations obtained above it follows that

$$2T_1 + V_1 = 2E_1 - V_1 = -Z^3\frac{\partial}{\partial Z}\left(\frac{E_1}{Z^2}\right).$$

Using Eq. (6) it follows that

$$\lambda Z\langle\exp(-\lambda r)\rangle = -Z^3\frac{\partial}{\partial Z}\left(\frac{E_1}{Z^2}\right).$$

If the approach of the total energy to the critical charge (keeping λ unchanged) is given by

$$E_1 \approx \alpha(Z - Z_c)^2$$

(case A), then, for $Z \approx Z_c$,

$$\lambda Z\langle\exp(-\lambda r)\rangle \approx -2\alpha Z_c(Z - Z_c),$$

which is consistent with Eq. (12).

III. THE TWO-ELECTRON YUKAWA ATOM

A. Review of earlier results

The two-electron Hamiltonian with Yukawa potential, Eq. (2), yields

$$E_2 = T_2 + V_2,$$

where

$$T_2 = \left\langle -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right)\right\rangle,$$

$$V_2 = \left\langle -Z\left(\frac{\exp(-\lambda r_1)}{r_1} + \frac{\exp(-\lambda r_2)}{r_2}\right) + \frac{\exp(-\lambda r_{12})}{r_{12}}\right\rangle.$$

This system has been investigated rather extensively. The observation that intrigued our curiosity is that the critical screening parameter at which the first electron detaches in the screened H^- ion is very close to that at which the remaining electron (i.e., in the screened hydrogen atom) becomes unbound [2–5]. In fact, the authors quoted above suggested that the two electrons may detach simultaneously. Fitting the binding energies given in [2] for the screened H and H^- atoms for the four highest values of the screening constants to cubic polynomials and extrapolating to vanishing binding energies we obtained the critical screening constants $\lambda_1^{(c)} \approx 1.173$ (which is a bit smaller than the best value quoted above, $\lambda_1^{(c)} \approx 1.191$) and $\lambda_2^{(c)} \approx 1.150$. While quite close to one another, these values suggest that the two electrons detach consecutively, not simultaneously, upon increasing the screening constant. The ground state as well as several excited states of the screened He atom were studied by Kar and Ho [20]. Extrapolating the He^+ energies one obtains $\frac{\lambda^{(c)}(He^+)}{2} \approx 1.17$. Similarly, $\frac{\lambda^{(c)}(He)}{2} \approx 1.14$. Winkler [2] points out that the binding energy decreases rather slowly upon increase of the screening parameter for both the one- and the two-electron systems, until the screening length, $D = \frac{1}{\lambda}$, becomes comparable to the Bohr radius of the $1s$ atom. Upon further increase of the screening constant the binding energies decrease rather rapidly. This observation, made also by Ugalde *et al.* [4], makes the proximity of the critical screening constants for the one- and the two-electron systems more plausible. Zhang and Winkler [3] claim that for the screened He atom the two electrons detach simultaneously at $\frac{\lambda_1^{(c)}}{2} = \frac{\lambda_2^{(c)}}{2} \approx 1.160$. This value is definitely lower than the best one-electron critical screening constant, quoted above.

B. The two-electron computational procedure

Two entirely independent computational procedures were applied for the Yukawa two-electron problem. Within the first procedure, that follows Hylleraas, the two-electron wave functions are expansions of the form

$$\psi = \exp(-\alpha s)\sum_k c_k s^{\ell_k} t^{m_k} u^{n_k},$$

where s, t, and u are the Hylleraas coordinates [21] defined by $s = r_1 + r_2, t = -r_1 + r_2$, and $u = r_{12}$. α and the c_ks are variational parameters determined by minimizing the calculated energy. The c_ks were found by solving the secular determinant and α was determined by hand optimization. The wave functions included all terms with $\ell_k + m_k + n_k \leqslant 13$ subject to the requirement that m_k is even. The resulting wave functions thus include 308 terms.

The second procedure employed, the Lagrange-mesh method [22,23], is a numerical procedure for solving the Schrödinger equation by placing it into a nonuniform inhomogeneous lattice defined by zeros of classical orthogonal polynomials, using a basis of Laguerre functions and the associated Gauss quadratures. The wave function is described in terms of the perimetric coordinates [24,25]

$$x = -r_1 + r_2 + r_{12},$$
$$y = r_1 - r_2 + r_{12},$$
$$z = r_1 + r_2 - r_{12},$$

which are defined over $[0,\infty]$. This computational procedure is reviewed in [26]. The numerical calculations are carried out using a straightforward modification of the PERILAG code written by Baye [22,23,26], that employs the JADAMILU fast diagonalization of large sparse matrices program [27]. For the present calculations, we have employed the lattice parameters [28] $N_x = N_y = 50$, $N_z = 40$ and the scaling parameters $h_x = h_y = 0.8$, $h_z = 0.5$.

The results are discussed in the following section. Here we just point out that the two computational procedures yield identical energies, to six decimals. Thus, for $Z = 1, \lambda = 0.5$ the Hylleraas-like wave function yields $E_2 = -0.15782627$ and the Lagrange-Laguerre–mesh method yields $E_2 = -0.15782642$.

C. Computational results

The binding energies of the second electron, i.e., the difference between the two-electron and the one-electron energies for common Z and λ, are plotted in Fig. 1 for constant Z, as functions of $\frac{\lambda}{Z}$. Note the different vertical scales used in order to fit all curves into a single figure.

In the following section we prove Lemma 2.

Lemma 2. The initial slope of $(E_1 - E_2)$ versus $\frac{\lambda}{Z}$, at constant Z, is $Z(1 - Z)$.

This lemma is consistent with the observation that for $Z > 1$ the dependence of the binding energy on the screening constant is monotonically decreasing, but for $Z < 1$ one notices the appearance of a maximum in the binding energy at some finite λ. Numerical evaluation of the slopes at $\frac{\lambda}{Z} = 0$ are in agreement with the lemma to six decimals, providing another confirmation of the accuracy of the computed energies. Hence, for $Z < 1$ screening enhances the binding of the second electron. This behavior suggests that for $Z < 1$ the reduction in the interelectronic repulsion due to the screening is more significant than the reduction in the nuclear attraction. This is particularly interesting at $Z < Z_c \approx 0.91102822407725573$, where the two-electron bare Coulomb atom ceases to be bound. Below this critical charge the two-electron system remains bound over a range of screening constants bounded by a lower and an upper critical screening constant. This range decreases upon further decrease of Z, eventually vanishing at some critical charge, below which no choice of parameters allows the two-electron system to be bound. We note that while the upper critical screening constant decreases rather slowly with decreasing Z, the lower critical screening constant increases fairly rapidly. Extrapolating the binding ranges to zero suggests that the lowest nuclear charge allowing binding, with appropriate screening, is roughly $Z_m \approx 0.676$. The maximal binding energies decrease rather rapidly upon lowering the nuclear charge and suggest a higher value of Z_m, perhaps as high as 0.688. The binding energies are possibly consistent with the lower value of Z_m estimated by extrapolation of the binding

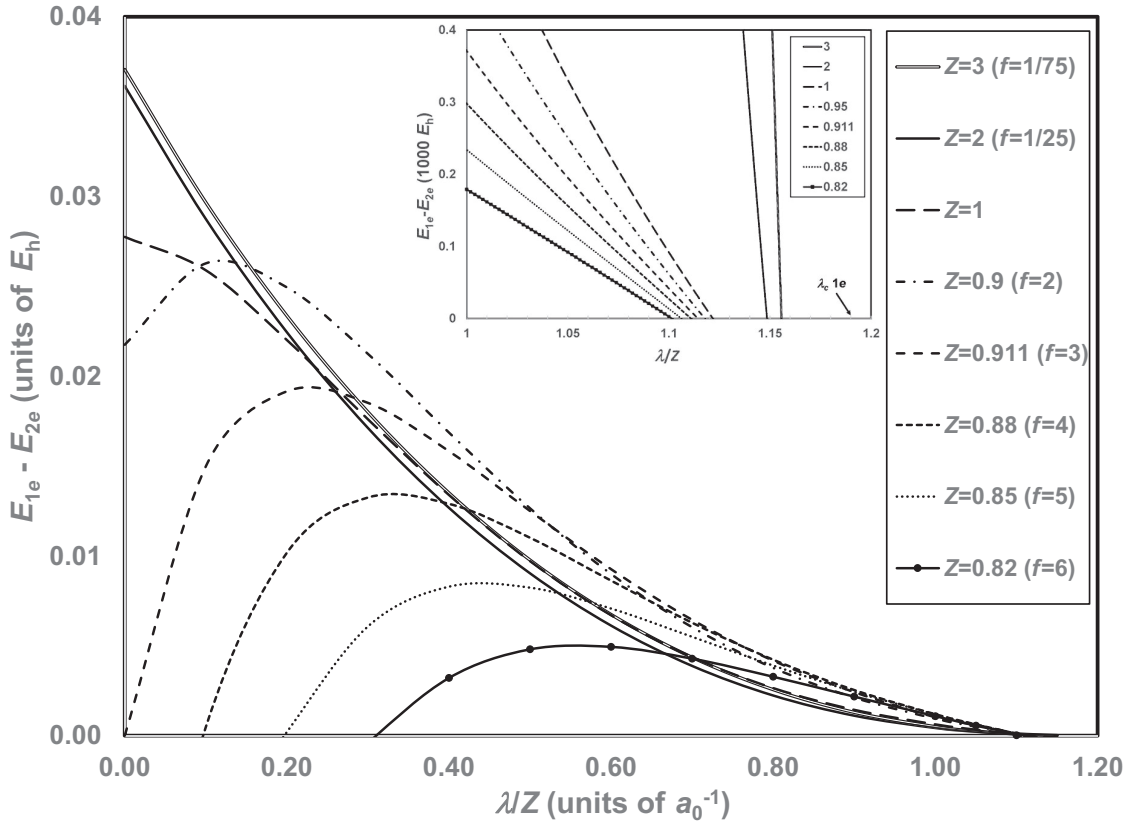

FIG. 1. Binding energy of the second electron. Inset: Extrapolations towards the critical screening constants. Note that the binding energies displayed in the main figure are multiplied by scaling factors (f), needed to fit all the curves into a common frame.

ranges, if their approach to zero is very slow. However, actually approaching this value would pose a significant computational challenge. We suggest $Z_m \approx 0.68$ as our best estimate of the lowest nuclear charge at which screening can yield a bound ground state. The limiting value of the screening constant at which binding is achieved at Z_m is roughly $\frac{\lambda}{Z_m} \approx 0.977$.

The inset in Fig. 1 shows the extrapolations that yield estimates of the critical screening constant, for the different values of Z. The one-electron critical screening constant, shown by the arrow towards the right end of the scale, is definitely higher than the two-electron critical screening constants, that approach it as $Z \to \infty$. At this limit the interelectronic repulsion becomes relatively insignificant.

D. The two-electron virial and Hellmann-Feynman theorems

The virial theorem [4,5,29] is obtained in complete analogy with the one-electron case, Eq. (6), yielding

$$2T_2 + V_2 = U,$$

where

$$U = \lambda\langle Z(\exp(-\lambda r_1) + \exp(-\lambda r_2)) - \exp(-\lambda r_{12})\rangle.$$

The Z-Hellmann-Feynman theorem is

$$\frac{\partial E_2}{\partial Z} = -\left\langle \frac{\exp(-\lambda r_1)}{r_1} + \frac{\exp(-\lambda r_2)}{r_2} \right\rangle,$$

and the λ-Hellmann-Feynman theorem is

$$\frac{\partial E_2}{\partial \lambda} = \langle Z(\exp(-\lambda r_1) + \exp(-\lambda r_2)) - \exp(-\lambda r_{12})\rangle = \frac{U}{\lambda}. \tag{13}$$

It follows that the two components of the potential energy are given by

$$v_{12} = \left\langle \frac{\exp(-\lambda r_{12})}{r_{12}} \right\rangle = 2E_2 - \lambda\frac{\partial E_2}{\partial \lambda} - Z\frac{\partial E_2}{\partial Z},$$
$$v = -Z\left\langle \frac{\exp(-\lambda r_1)}{r_1} + \frac{\exp(-\lambda r_2)}{r_2} \right\rangle = Z\frac{\partial E_2}{\partial Z}.$$

Hence,

$$V_2 = v + v_{12} = 2E_2 - \lambda\frac{\partial E_2}{\partial \lambda} = -\lambda^3\frac{\partial}{\partial \lambda}\left(\frac{E_2}{\lambda^2}\right), \tag{14}$$

and

$$T_2 = -E_2 + \lambda\frac{\partial E_2}{\partial \lambda} = \lambda^2\frac{\partial}{\partial \lambda}\left(\frac{E_2}{\lambda}\right).$$

Just like the one-electron case discussed above, the virial ratio $-\frac{V_2}{T_2}$ approaches unity upon approaching the critical screening constant.

Combining Eqs. (9) and (14) we obtain

$$V_2 - V_1 = 2(E_2 - E_1) - \lambda \frac{\partial (E_2 - E_1)}{\partial \lambda} = -\lambda^3 \frac{\partial}{\partial \lambda}\left(\frac{E_2 - E_1}{\lambda}\right).$$

In the vicinity of the two-electron critical point the binding energy of the second electron is asymptotically given by

$$E_2 - E_1 \approx a\left(\lambda_2^{(c)} - \lambda\right)^{\zeta},$$

so that

$$V_2 - V_1 \approx 2a\left(\lambda_2^{(c)} - \lambda\right)^{\zeta} - \lambda\zeta a\left(\lambda_2^{(c)} - \lambda\right)^{\zeta - 1}.$$

If $\zeta = 2$ then $V_2 - V_1$ vanishes at $\lambda = \lambda_2^{(c)}$, implying that one of the electrons becomes infinitely diffuse. However, if $\zeta = 1$ then $V_2 - V_1 = -\lambda_2^{(c)} a$, which means that the two-electron wave function is bound at the critical point.

We are now ready to prove Lemma 2.

Proof. Using Eqs. (8) and (13) we obtain

$$\frac{\partial}{\partial \lambda}(E_1 - E_2) = Z(\langle \exp(-\lambda r)\rangle_1 - \langle \exp(-\lambda r_1) + \exp(-\lambda r_2)\rangle_2) + \langle \exp(-\lambda r_{12})\rangle_2,$$

where $\langle \hat{o} \rangle_1$ stands for the expectation value of the operator $\hat{o}$ with respect to the one-electron wave function, and $\langle \hat{O} \rangle_2$ stands for the expectation value of $\hat{O}$ with respect to the two-electron wave function. At $\lambda = 0$ this expression simplifies into

$$\frac{\partial}{\partial \lambda}(E_1 - E_2) = -Z + 1.$$

Hence, the slope of $(E_1 - E_2)$ versus $\frac{\lambda}{Z}$ is $Z(1 - Z)$. ■

A numerical examination of the virial-Hellmann-Feynman relations presented above allows a further assessment of the accuracy of the computational results. Evaluating $E_2(Z,\lambda = 0.5)$ for $Z = 0.996, 0.998, 1.000, 1.002, 1.004$ and using a five-point estimate of $\frac{\partial E_2}{\partial Z}$ we obtain $\frac{\partial E_2}{\partial Z}|_{Z=1,\lambda=0.5} = -0.617702$. A similar procedure yields $\frac{\partial E_2}{\partial \lambda}|_{Z=1,\lambda=0.5} = 0.493644$. Using these numerical estimates we obtain

$$v = Z\frac{\partial E_2}{\partial Z} = -0.617702,$$

$$U = \lambda \frac{\partial E_2}{\partial \lambda} = 0.246822,$$

$$V_2 = 2E_2 - \lambda \frac{\partial E_2}{\partial \lambda} = -0.562475,$$

$$T_2 = -E_2 + \lambda \frac{\partial E_2}{\partial \lambda} = 0.404648.$$

The expectation values evaluated with the 308-term Hylleraas-type wave function agree with the values presented above to all decimals presented.

It is of some interest to explore, more closely, the behavior of the binding energy, $E_1 - E_2$, as a function of Z and λ, in the vicinity of (Z_m,λ_m), where Z_m is the lowest nuclear charge allowing a bound two-electron state, and λ_m is the value of the screening parameter that gives rise to binding of the two electrons at Z_m. Using the one- and two-electron Z- and λ-Hellmann-Feynman theorems we obtain

$$\left.\frac{\partial}{\partial \lambda}(E_1 - E_2)\right|_{(Z_m,\lambda_m)} = Z\langle \exp(-\lambda r)\rangle_1 - \langle Z(\exp(-\lambda r_1) + \exp(-\lambda r_2)) - \exp(-\lambda r_{12})\rangle_2,$$

$$\left.\frac{\partial}{\partial Z}(E_1 - E_2)\right|_{(Z_m,\lambda_m)} = -\left\langle \frac{\exp(-\lambda r)}{r}\right\rangle_1 + \left\langle \frac{\exp(-\lambda r_1)}{r_1} + \frac{\exp(-\lambda r_2)}{r_2}\right\rangle_2,$$

where $\langle \cdots \rangle_1$ and $\langle \cdots \rangle_2$ are expectation values with respect to the one-electron and the two-electron wave functions, respectively. Our best approximation to (Z_m,λ_m) is $(0.68, 0.6643)$. At this point we have

$$E_1 = -0.0060010 \quad E_2 = -0.0060094,$$

$$Z\langle \exp(-\lambda r)\rangle_1 = 0.08406 \quad \langle Z(\exp(-\lambda r_1) + \exp(-\lambda r_2)) - \exp(-\lambda r_{12})\rangle_2 = 0.08409,$$

$$\left\langle \frac{\exp(-\lambda r)}{r}\right\rangle_1 = 0.0998 \quad \left\langle \frac{\exp(-\lambda r_1)}{r_1} + \frac{\exp(-\lambda r_2)}{r_2}\right\rangle_2 = 0.1008.$$

The first pair, (E_1, E_2), indicates how close we are to a vanishing binding energy. The second pair, $(\frac{\partial E_1}{\partial \lambda}, \frac{\partial E_2}{\partial \lambda})$, indicates how close we are to a minimum with respect to λ, and the third pair, $(\frac{\partial E_1}{\partial Z}, \frac{\partial E_2}{\partial Z})$, indicates that at (Z_m,λ_m) the first derivative of the binding energy with respect to Z vanishes. This last fact implies that upon approaching Z_m, the binding energy depends quadratically on $(Z - Z_m)$, suggesting a two-electron wave function that "expands" (becomes infinitely diffuse).

IV. CONCLUDING REMARKS

The computations presented in the present paper were verified, to high accuracy, by running independent numerical procedures for both the one- and the two-electron systems. Furthermore, identities obtained using the virial theorem and two varieties of the Hellmann-Feynman theorem were verified numerically, providing further assessment of the computational procedures.

TABLE I. First and second critical screening constants for the $2p^2\,{}^3P$ state.

Z	$\lambda_c(2p^2\,{}^3P)/Z$	$\lambda_c(2p)/Z$
2	0.1771	0.213
3	0.1957	0.215
4	0.1996	0.214
5	0.2064	0.217
6	0.2023	0.212

In the two-electron systems two distinct critical screening constants were evaluated, at the lower of which one of the electrons and at the higher of which the remaining electron is detached. For $Z < 1$ a moderate amount of screening was demonstrated to increase the binding energy of the second electron, further screening eventually lowering its binding energy, until it is detached at some critical value of the screening parameter. While $Z < 1$ does not correspond to a physically realizable system, the presently reported observation is of interest in a mathematical physics sense, indicating a rather counterintuitive feature of two-particle binding. Moreover, it is conceivable that analogous effects could take place in heavier atoms at realistic values of Z. Careful attention is required for the evaluation of electron affinities of atoms in plasmas.

An interesting set of expectation values involving the ground state of the screened He atom is presented by Jiao and Ho [30]. The virial ratio $-\frac{V_2}{T_2}$ decreases from its unscreened value, 2, all the way to 1 upon approaching the critical screening constant, as anticipated above. The expectation values $\langle\frac{1}{r_1}\rangle$, $\langle r_1\rangle$, and $\langle r_1^2\rangle$, as well as $\langle\frac{1}{r_{12}}\rangle$, $\langle r_{12}\rangle$, and $\langle r_{12}^2\rangle$ are consistent with an expanding wave function upon approaching the critical screening constant. Even more revealing are the values of $\langle r_<\rangle$ and $\langle r_>\rangle$, the ratio $\frac{\langle r_>\rangle}{\langle r_<\rangle}$ slowly growing from ∼2.086 for the unscreened He ground state to ∼2.277 for $\lambda = 1$, thereafter rising rapidly upon further increase of λ towards $\lambda_2^{(c)}$.

Analyzing the data in [31,32] for the $2p^2\,{}^3P$ state, for $Z = 2,3,4,5,6$, we obtain the results presented in Table I. We denote the screening constant that corresponds to the ionization of the first electron by $\lambda^{(c)}(2p^2\,{}^3P)$, and the screening constant that corresponds to the ionization of the remaining electron by $\lambda^{(c)}(2p)$. We note that $\frac{\lambda^{(c)}(2p)}{Z}$, that should have been constant, shows some scatter at the third digit, that indicates the accuracy achieved in the evaluation of this constant. We take the average, 0.214, as the "definitive" value. This critical screening parameter is clearly larger than $\frac{\lambda^{(c)}(2p^2\,{}^3P)}{Z}$, the latter being (almost) monotonically increasing with increasing Z (the $Z = 6$ value must be inaccurate). Hence, upon increasing the screening constant the first $2p$ electron detaches before the second one does. Graphical extrapolation of $\frac{\lambda^{(c)}(2p^2\,{}^3P)}{Z}$ to $\frac{1}{Z} \to 0$ yields

$$\lim_{\frac{1}{Z}\to 0} \frac{\lambda^{(c)}(2p^2\,{}^3P)}{Z} \approx 0.215,$$

which is reasonably close to the average value of $\frac{\lambda^{(c)}(2p)}{Z}$, specified above. This just means that at large Z correlation becomes insignificant and the two electrons are asymptotically detached together.

The sequential, rather than simultaneous, detachment of the electrons in the doubly excited state, $2p^2\,{}^3P$, of H^- and in the triply excited states $1s2s2p\,{}^4P$ and $2p^3\,{}^4S$ of He^- upon increasing the screening parameter had already been reported by Mercero *et al.* [5].

While the systems we investigate ($Z \sim 1$) are too light to exhibit significant relativistic effects, there may possibly be subtle relativistic modifications of the behavior at the critical points, that are beyond the scope of the present paper.

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