Bound Eigenstates of the Static Screened Coulomb Potential*

F. J. Rogers, H. C. Graboske, Jr., and D. J. Harwood
Lawrence Radiation Laboratory, University of California, Livermore, California 94550
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Accurate numerical solutions have been obtained for Schrödinger's equation for a two-particle system interacting through a static screened Coulomb potential (SSCP) $V(r) = -Ze^2e^{-r/D}/r$. The numerical integration of the wave equation uses a one-dimensional difference method which is simple, accurate, and efficient. Solutions have been computed for 45 eigenstates, 1s through $n=9$, $l=8$, yielding the eigenfunctions and energy eigenvalues for a wide range of D, the screening length which characterizes the range of the interaction. Under screening, all energy levels are shifted away from their unscreened values toward the continuum, the energy increasing as D decreases. For each n, l eigenstate, there is a finite value of the screening length $D_0(n,l)$, for which the energy becomes zero. The value of D_0 for the ground state of a two-particle bound system in a potential of this type, such as the Debye or Yukawa potential, is $0.83991\ a_0/Z$ in agreement with certain previous studies. The total number of different energy levels is finite for any finite D, and is approximately linearly dependent on D. The number of bound s states g^* is given by the relation $(g^*)^2 = 1.2677\ DZ/a_0$. For given n, the l degeneracy is destroyed, lowest l levels lying lowest in energy. At sufficiently high n, this behavior results in level crossing, high l levels of eigenstate n having higher energies than low l levels of eigenstate $n+1$. This produces increasingly complex deviations of the level order from the unscreened order, commencing with the 5s-4f crossover. Because of the displacement of high n states into the continuum, the density of states in the SSCP for any finite D is lower than in the unscreened potential, especially near the continuum.

I. INTRODUCTION

The problem of finding the energy levels (or at least the number of them) of a hydrogenic atom in an ionized gas has received the attention of a number of authors[1-6] in the past. The present authors became interested in this problem through a need to calculate the partition function for such hydrogenic atoms. The partition function for the isolated hydrogen atom, given by

$$Z = \sum_{n=1}^{\infty} 2n^2 \exp\left(\frac{Ry}{n^2kT}\right), \tag{1.1}$$

clearly diverges. In any real physical situation, of course, the atom is not truly isolated and the upper bound levels will be perturbed into the continuum of unbound states by even a very small interaction.

The partition function is then given by a finite sum. The upper limit of this sum g^*, the maximum bound principal quantum number, has been calculated previously in various approximations. We give it below as very nearly proportional to the square root of the screening length. It is also important to note that a knowledge of g^* alone does not merit the importance that has sometimes been attached to it since in order to calculate the partition function one needs to know not only the number of energy levels (including their degeneracy) but also how the energy eigenvalues vary as a function of the screening length. These energy eigenvalues for some of the lower-lying states (the most important ones for calculation of a partition function) have been calculated, and the results are presented here.

II. QUALITATIVE DISCUSSION OF THE SPECTRUM

The radial Schrödinger equation for this problem is given by

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{d}{dr}r^2\frac{d}{dr} - \frac{l(l+1)}{r^2}\right) \times R(r) + V(r)R(r) = E\,R(r)\,. \tag{2.1}$$

Several forms have been suggested for the shielded Coulomb potential of an atom surrounded by a plasma. The two basic forms are the static screened Coulomb (Debye) potential (SSCP)[3]

$$V(r) = -(Ze^2/r)e^{-r/D}, \tag{2.2a}$$

and the shifted SSCP,[1,7]

$$V(r) = -(Ze^2/r)\,e^{-r/D} - e^2/D\ , \tag{2.2b}$$

where D is the screening length. Although the difference in the statistical machanics of the gas can be significant for these two forms,[7] the solutions to the Schrödinger equation are equivalent.

The resultant eigenvalues for the shifted SSCP differ by a constant term $-e^2/D$ from those for the SSCP. In the following analysis, we refer to the first form [Eq. (2.2a)].

The potential is effectively restricted to a range of the order of D. When D is large we say that the screening is weak, and when D is small the screening is strong. In plasma theory, the screening length is called the Debye screening length and is given by

$$D=\left(\frac{4\pi}{kT}\sum_j \rho_j e^2 Z_j^2\right)^{-1/2},$$

where T is the temperature of the ionized gas, ρ_j is the density of particles of type j, and $e\,Z_j$ is the charge. This potential is the same as that of Rouse[6] in the case that A (his "mean minimum radius of the ion atmosphere") is set to zero.

By making the substitutions,

$$r=a_0x/Z,\quad D=a_0\delta/Z,$$
$$\text{and}\quad E=Z^2e^2\epsilon/(2a_0), \tag{2.3}$$

where $a_0=\hbar^2/m\,e^2$, Eq. (2.1) may be written in the form

$$\frac{d^2R}{dx^2}+\frac{2}{x}\frac{dR}{dx}+\left(\epsilon+\frac{2}{x}\,e^{-x/\delta}-\frac{l(l+1)}{x^2}\right)R=0. \tag{2.4}$$

For very large values of δ, the eigenvalues ϵ_n of this equation are expected to be very little different from those of the isolated hydrogen atom for which $\epsilon_n=-n^{-2}$. If we expand the exponential to first order, $e^{-x/\delta}\approx 1-x/\delta$, Eq. (2.4) looks like the equation for an isolated hydrogenic atom with ϵ replaced by $\epsilon-2/\delta$, or from (2.3), the energy will contain an additive term Z^2e^2/D. In other words, the first-order effect of the screening is to simply add the constant energy term Z^2e^2/D to each energy level. Of course, the uppermost states will be raised above the ionization energy and we see right away that even for very large screening lengths, the problem has changed from one with an infinite number of bound states to one with a finite number of bound states.

This same result may be shown by means of a classical approximation, valid for large radial quantum numbers. If the force derived from the potential (2.2) is set equal to the mass times the centripetal acceleration v^2/r, we see

$$m\,v^2/r=(Ze^2/r^2)\,(r+D)/D\,e^{-r/D}. \tag{2.5}$$

The total energy is

$$E=\tfrac{1}{2}mv^2-(Ze^2/r)e^{-r/D}, \tag{2.6}$$

or substituting from (2.5), we find

$$E=-(Ze^2/2r)\,(D-r)/D\,e^{-r/D}. \tag{2.7}$$

This expression clearly recovers the correct energy value for infinite screening length, and in fact if an expansion is made in r/D we see

$$E=-Ze^2/2r+Ze^2/D-\cdots, \tag{2.8}$$

which shows the same first-order correction to the energy as was obtained previously. Moreover, it is apparent from (2.7) that for sufficiently small values of D (D less than approximately the average orbit radius), the energy of these high-lying states cannot be negative. Thus, we see again that the upper levels will all be cut off at some critical value of the screening length $D_0(n,l)$, and the number of energy levels will be finite. This critical screening length at which a level is cut off is $D_0\sim\bar{r}$, where $\bar{r}$ is the average orbit radius. For the hydrogenic atom with no screening, $\bar{r}\sim a_0n^2/Z$. Thus, replacing n by g^*, the maximum-bound principal quantum number, we expect $D_0\sim a_0g^{*2}/Z$.

It can be shown[8] by an elementary argument utilizing the uncertainty principle that any attractive potential which approaches zero faster than $-r^{-2}$ as r approaches infinity can have, at most, a finite number of energy levels. The screened Coulomb potential (2.2a) certainly qualifies in this respect. This conclusion that only a finite number of energy levels exist for finite screening is contrary to a recently published report of Rouse.[6]

If in Eq. (2.4) we substitute

$$u(x)=x\,R(x), \tag{2.9}$$

it becomes

$$u''+\left(\frac{2}{x}\,e^{-x/\delta}+\epsilon-\frac{l(l+1)}{x^2}\right)u=0, \tag{2.10}$$

which may be regarded as a one-dimensional Schrödinger equation with an effective potential $l(l+1)/x^2-(2/x)e^{-x/\delta}$. It is easily shown[9] that for a given value of l the energy eigenvalues ϵ_{nl} are not n degenerate. It is also expected that the accidental degeneracy peculiar to the Coulomb potential will be destroyed for any finite value of the screening length and hence the energy will depend upon the azimuthal quantum number l. As for all central potentials, the energy is independent of the magnetic quantum number m [it does not appear in Eq. (2.4)], and hence the energy levels will have degeneracy $2l+1$.

III. NUMERICAL METHOD

We are interested in obtaining an accurate solution of Eq. (2.1). It has been pointed out[5] that

approximate analytic solutions involve considerable numerical work while yielding accurate results only for restricted ranges of n, l, and D. For this reason we use a direct numerical approach.

A numerical solution in r space would present some difficulties, as solutions for a given (n, l) state do not exist for $D < D_0(n, l)$, as demonstrated above, where $D_0(n, l)$ is some unknown positive critical screening length. Consider the transformations[6]

$$\rho = (2Z/a_0)\, r/\lambda_{n,l} \quad ,$$
$$\epsilon_{n,l} = -Z^2\hbar^2/2\, a_0^2\, \mu\, \lambda_{n,l}^2 \, , \tag{3.1}$$
$$d = (2Z/a_0)\, D/\lambda_{n,l} \quad ,$$

where $\lambda_{n,l}$ is the eigenvalue of the radial Schrödinger equation in ρ space, and d is the transformed screening length. The transformed form of Eq. (2.1) is

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left(\frac{\lambda_{n,l}\, e^{-\rho/d}}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right) R = 0. \tag{3.2}$$

This transformation maps the range $D_0 \leq D \leq \infty$ of the screening length into the range $0 \leq d \leq \infty$ of the transformed screening length. This is evident, since $\epsilon_{n,l} = 0$ only if $\lambda_{n,l} = \infty$ for which value $d = 0$. Therefore, solutions of Eq. (3.2) with discrete eigenvalues exist for all $d > 0$, and the cutoff value of the screening length for any particular state can be systematically determined by assigning successively smaller values to d and extrapolating to find $\lim(D)$ as $d \to 0$. For these reasons, we find solutions to Eq. (3.2) and convert the results according to Eq. (3.1).

A simple linear difference equation was found to produce stable, accurate, computationally fast solutions to the radial Schrödinger equation. Specifically, the derivatives were replaced by

$$\frac{dR_i}{d\rho} = \frac{R_{i+1} - R_{i-1}}{2\Delta\rho} \quad ,$$
$$\frac{d^2R_i}{d\rho^2} = \frac{R_{i+1} + R_{i-1} - 2R_i}{(\Delta\rho)^2} \, ,$$

where i is the space index. The resulting difference equation for the wave amplitude is

$$R_{i+1} = 1/(i+1)\{-(i-1)R_{i-1} + [i(2 + \tfrac{1}{4}(\Delta\rho)^2) + l(l+1)/i - \lambda_{n,l}\Delta\rho e^{-\rho/d}]R_i\}. \tag{3.3}$$

The starting condition for s states is obtained by noting that as $\rho \to 0$, Eq. (3.2) has the asymptotic solution $R = 1 - \frac{1}{2}\lambda_{nl}\rho$, where $R(0)$ has been chosen equal to unity. For $l > 0$, $R(0) = 0$ so that $R(\Delta\rho) = R_1$ is arbitrary. A convenient choice is $R_1 = (\Delta\rho)^l$. The boundary condition $R = 0$ at $r = \infty$ is of necessity replaced by the condition $R = 0$ at $r = r_0$ which takes the form $\rho_0 = 2Zr_0\lambda_{n,l}a_0$ in ρ space. Note that for a constant ρ_0, the corresponding $r_0 \to \infty$ as $\lambda_{n,l} \to \infty$.

An eigenvalue of the difference Eq. (3.3) will have the characteristic that the values of $R(\rho_0)$, obtained if $\lambda_{n,l}$ is incremented by $\pm\epsilon$, will have opposite sign. The searching procedure to find values of λ_{nl} which satisfy this condition can be systematized for a given l and d by checking for changes in sign of $R(\rho_0)$ for successively increasing values of $\lambda_{nl} = \lambda_0$, $\lambda_0 + \Delta\lambda$, $\lambda_0 + 2\Delta\lambda, \cdots$, with $\lambda_0 \approx l + 1$, where $\Delta\lambda$ is smaller than the eigenvalue spacing obtained with a larger value of d. In this way, the eigenvalues $\lambda_{l+1,l}^{(d)}$, $\lambda_{l+2,l}^{(d)}$ are bracketed within a range $\Delta\lambda$. An iterative quadratic root-solving method is then used to isolate the eigenvalue to the desired accuracy. The long-range tail of the Coulomb potential is exponentially damped at large ρ so that for small d the potential becomes short range. For this reason, the numerical solution uses a variable step size, $\Delta\rho$ being smaller near the origin than at large values of ρ.

In the calculation of each wave function a total of 4000 steps were taken, except near the continuum where about 20 000 steps were taken. The first 2000 steps were approximately of magnitude $\Delta\rho = 0.005d$ if $d \leq 1$; otherwise they were approximately $\Delta\rho = 0.005$. The second 2000 steps were an integer multiple of the initial step size and were approximately of magnitude $\Delta\rho = 0.015$. To ensure that the value chosen for ρ_0 did not affect the accuracy of the solution, ρ_0 was moved out 10% by increasing the number of steps. Next, to ensure that the chosen step sizes were sufficiently small to produce negligible error, they were decreased 10%, keeping the boundary at the larger radius. In all cases, it was found that the three eigenvalues agreed to at least five significant figures.

The procedure outlined above was tested on three problems which have exact analytic solutions — the harmonic oscillator, the hydrogen atom, and the hydrogen atom confined to a spherical box of radius r_0. In all cases, excellent agreement with the analytic solutions was obtained. In particular, seven-place accuracy was obtained for the hydrogen atom to quite large values of n and l. The confined atom problem, solved analytically by DeGroot and ten Seldam,[10] is obviously a limiting version of the present SSCP problem for $D \to \infty$. The confined atom has as radial eigenfunctions the confluent hypergeometric functions, and the energy levels are perturbed in a manner similar to the SSCP levels.

The choice of r_0 must be made carefully, to ensure that the perturbation due to confinement is not a factor in the present problem. As noted earlier, when the calculations are performed in ρ space the boundary r_0 automatically moves out as λ_{nl} increases for a constant value of ρ_0. It was found that sufficiently large values of ρ_0 could always be chosen from the range 20–60, with the lower values of ρ_0 being used with the high screening or low n and the larger values with low screening or high n.

Other studies[11] have claimed that this approach is unsatisfactory and have consequently gone to more elaborate numerical methods which use Taylor series expansions around the origin, high-order difference equations, and match the numerical solution to the asymptotic solution for large r. A major reason for this disagreement seems to be that the previous studies have used a constant step size throughout the entire calculation.

These calculations were performed on a CDC 6600 computer, a 14-digit machine, at the rate of 54 eigenvalues per min. To ensure that round-off and/or truncation errors were not important, a few duplicate calculations were made on a CDC 3600 computer, a 10-digit machine (and also slower as only 14 eigenvalues were calculated per min). These calculations were in agreement with the CDC 6600 results.

IV. RESULTS

The results of applying this numerical technique to the problem of the SSCP are in agreement with the theoretical conculsions presented above. In what follows, except where indicated, the results and conclusions refer to real space (r space). The normalized probability density distribution $[r^2R^2_{n,l}(r)]$ for the $3p$ state is illustrated in Fig. 1 for four values of the screening length. The largest value $DZ/a_0=\infty$ corresponds to the unscreened case; the intermediate value $DZ/a_0=50$ represents the weak screening case, while the smallest values $DZ/a_0=20$ and 10 are strongly screened atoms.

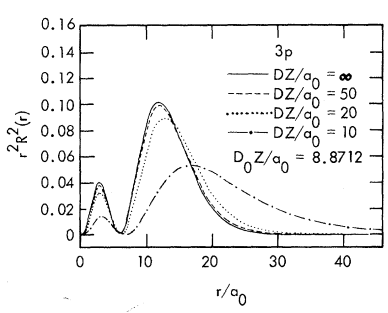

FIG. 1. $|rR_{31}(r)|^2$ versus r for various screening lengths.

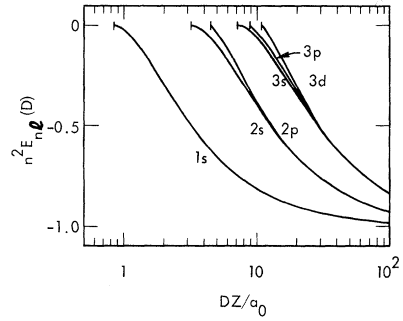

FIG. 2. Dependence of the energy levels on the screening lengths for the six lowest-lying states.

The expected features are present: The density distribution is shifted away from the origin, and the peak values are reduced, both effects increasing with decreasing D. It should be noted that the normalized radical density distribution is changed by a relatively small amount at values of D where the energy eigenvalue is strongly perturbed.

The eigenvalues and energy levels were computed over a wide range of D for 45 one-electron eigenstates. The energy levels of the SSCP show a strong dependence on D, and agree with the qualitative dependence first demonstrated by Harris's perturbation and variational solutions[3] to the problem. The numerical solutions also verify that there is a critical value for D, below which there is no stable two-particle configuration with negative energy. This disappearance of the bound states in the limit of strong screening exhibits some well-defined regularities which will be discussed below.

The destruction of the l degeneracy of the unscreened-case results in SSCP eigenstates of lowest l (for a given n) lying lowest in energy. The states of different l for a specific value n vanish (are perturbed into the continuum) in inverse order of their l value.

The energies of the first six eigenstates are plotted in Fig. 2. The long-range nature of the screening perturbation is exhibited by the fact that the lowest-lying states are perturbed by more than 1% at ranges of the order of hundreds of angstroms. The energies of these six states are tabulated in Table I for a range of D. These numerical results demonstrate that the lower l states not only have the lowest energy at a chosen D, but they also have the smallest slope $\partial E_{n,l}/\partial D$ near the continuum. This increasingly steep gradient as l increases results in crossing of levels at sufficiently high values of n. In Fig. 2, the vertical lines at $E=0$ indicate the critical values of D at which $E_{n,l}(D)$ for each state goes to zero.

The energies of the eigenstates $4s$ through $9l$ are tabulated in Table II. It will be seen that in

TABLE I. Eigenstate energy as a function of screening length for the 1s, 2s, 2p, 3s, 3d, and 3d states.

ZD/a_0	1s	2s	2p	3s	3p	3d
∞	1.0000	0.2500	0.2500	0.1111	0.1111	0.1111
500	0.9960	0.2460	0.2460	0.1072	0.1072	0.1072
200	0.9900	0.2401	0.2401	0.1014	0.1014	0.1014
100	0.9801	0.2306	0.2305	0.092 40	0.092 31	0.092 12
70	0.9717	0.2226	0.2224	0.085 12	0.084 94	0.084 57
50	0.9606	0.2123	0.2119	0.076 04	0.075 70	0.075 03
40	0.9509	0.2036	0.2030	0.068 66	0.068 16	0.067 15
30	0.9350	0.1895	0.1886	0.057 44	0.056 62	0.054 94
20	0.9036	0.1635	0.1615	0.038 70	0.037 12	0.033 83
15	0.8731	0.1400	0.1366	0.024 31	0.021 95	0.016 95
10	0.8141	0.099 86	0.093 07	0.00642	0.003 18	
7	0.7424	0.059 94	0.048 45	0.003 18		
5	0.6536	0.024 21	0.008 20			
4	0.5818	0.006 79				
3	0.4737					
2	0.2962					
1.4	0.1351					
1	0.020 57					

the weak screening regions, the various l levels for a given principal quantum number lie fairly close together. As the levels approach the continuum, the energy of different l levels varies markedly with D. The behavior of some higher levels is plotted in Fig. 3. Here the gradual approach to the continuum of the lower l levels causes a significant amount of level crossing, leading to a very complex ordering of the states near the continuum, and to a fairly large separation in energy between states of highest and lowest l for a given n.

Several previous studies have investigated the problem of the SSCP. Harris[3] used several approximate analytic methods to study the problem and established the correct qualitative behavior of the system, as well as accurate quantitative energies in the weak screening case. The agreement of the approximate analytic results for moderate to strong screening with the numerical results is rather poor for all states other than the $n, l = n-1$ levels, due to the inherent difficulties of using perturbation methods for high-lying levels and variational techniques for levels other than the most tightly bound state of given l.

Rouse used a different numerical technique[11] to calculate the first accurate solutions[6] for the $1s-3d$ states. For these states, at a value of $A = 0$, the two different numerical solutions agree extremely well, the maximum difference in energy being 1 part in 10^3, the average difference being approximately 1 part in 10^4. Although the two sets of published results agree almost completely, there is a substantial disagreement in the interpretation of the results beyond the smallest D values published by Rouse. Rouse only notes that the energy of each level goes to zero in the limit of $d \to 0$. But this does not imply that the states exist as $D \to 0$, and in fact one finds that in r space, the energy goes to zero at some finite nonzero value of the screening length $D_0(n, l)$. For $D < D_0$, the eigenstate cannot be formed with negative energy.

An approximate analytic solution of the SSCP problem has been presented by Smith,[4] who used perturbation theory to compute a first-order perturbation correction to the unscreened case for the limit of weak screening. This result yields an analytic energy-level correction which contains inverse powers of D and a factor involving the hypergeometric function. This model gives energy corrections which are approximately correct, as shown in Fig. 4. Here the difference between the numerical and analytic results is presented for the six lowest eigenstates. The analytic expression for the 1s state is extremely good, giving the energy to better than 1% accuracy for all $DZ/a_0 \geq 3$. The higher levels $n \geq 2$ are considerably less accurate, achieving numerical agreement better than 1% only for $DZ/a_0 \geq$ several hundred units. The discrepancy is essentially independent of l until D is close to the critical value D_0, indicating the analytic l dependence is correct. A second ana-

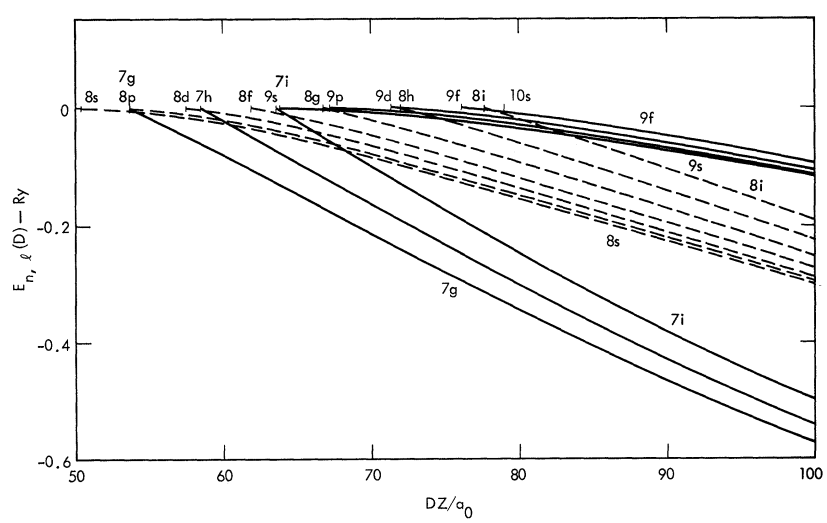

FIG. 3. Dependence of the energy levels on the screening length for some of the higher-lying states showing crossover of energy levels.

TABLE II. Eigenstate energy[a] as a function of screening length for the 4*s*–9*l* states.

State \ ZD/a_0	∞	1500	1000	700	500	400	300	200	150	100	70	50	40	30	20
4*s*	0.6250	0.6118	0.6052	0.5969	0.5859	0.5765	0.5609	0.5307	0.5018	0.4471	0.3831	0.3076	0.2501	0.1701	0.0618
4*p*	0.6250	0.6118	0.6052	0.5969	0.5859	0.5764	0.5608	0.5305	0.5014	0.4463	0.3814	0.3047	0.2459	0.1638	0.0520
4*d*	0.6250	0.6118	0.6052	0.5969	0.5858	0.5763	0.5606	0.5301	0.5006	0.4445	0.3782	0.2988	0.2374	0.1507	0.0316
4*f*	0.6250	0.6117	0.6052	0.5968	0.5857	0.5761	0.5603	0.5294	0.4993	0.4420	0.3732	0.2898	0.2244	0.1302	
5*s*	0.4000	0.3868	0.3804	0.3722	0.3615	0.3523	0.3373	0.3088	0.2820	0.2332	0.1792	0.1206	0.0805	0.0337	
5*p*	0.4000	0.3868	0.3804	0.3722	0.3614	0.3522	0.3372	0.3086	0.2816	0.2324	0.1778	0.1182	0.0773	0.0296	
5*d*	0.4000	0.3868	0.3803	0.3721	0.3613	0.3521	0.3370	0.3081	0.2809	0.2308	0.1749	0.1134	0.0708	0.0212	
5*f*	0.4000	0.3868	0.3803	0.3721	0.3612	0.3519	0.3367	0.3075	0.2797	0.2285	0.1705	0.1060	0.0607		
5*g*	0.4000	0.3868	0.3803	0.3720	0.3611	0.3517	0.3363	0.3066	0.2782	0.2253	0.1646	0.0957	0.0465		
6*s*	0.2778	0.2647	0.2583	0.2503	0.2399	0.2310	0.2167	0.1901	0.1658	0.1235	0.0802	0.0391	0.0163	0.0005	
6*p*	0.2778	0.2647	0.2583	0.2503	0.2398	0.2309	0.2167	0.1899	0.1655	0.1228	0.0790	0.0373	0.0143		
6*d*	0.2778	0.2647	0.2583	0.2502	0.2397	0.2308	0.2165	0.1895	0.1648	0.1214	0.0766	0.0337	0.0102		
6*f*	0.2778	0.2647	0.2582	0.2502	0.2396	0.2307	0.2162	0.1889	0.1637	0.1193	0.0730	0.0281	0.0040		
6*g*	0.2778	0.2646	0.2582	0.2501	0.2395	0.2304	0.2158	0.1880	0.1623	0.1165	0.0679	0.0204			
6*h*	0.2778	0.2646	0.2582	0.2500	0.2393	0.2301	0.2153	0.1870	0.1605	0.1128	0.0614	0.0101			
7*s*	0.2041	0.1911	0.1848	0.1769	0.1668	0.1584	0.1449	0.1204	0.0988	0.0634	0.0311	0.0071	0.0001		
7*p*	0.2041	0.1911	0.1848	0.1769	0.1668	0.1583	0.1448	0.1202	0.0985	0.0628	0.0302	0.0060			
7*d*	0.2041	0.1911	0.1848	0.1769	0.1668	0.1582	0.1447	0.1198	0.0978	0.0616	0.0283	0.0038			
7*f*	0.2041	0.1910	0.1847	0.1768	0.1667	0.1581	0.1444	0.1192	0.0969	0.0598	0.0254	0.0007			
7*g*	0.2041	0.1910	0.1847	0.1768	0.1665	0.1578	0.1440	0.1184	0.0956	0.0573	0.0215				
7*h*	0.2041	0.1910	0.1847	0.1767	0.1663	0.1576	0.1435	0.1174	0.0930	0.0541	0.0163				
7*i*	0.2041	0.1910	0.1846	0.1766	0.1661	0.1572	0.1429	0.1162	0.0919	0.0502	0.0097				
8*s*	0.1563	0.1433	0.1372	0.1295	0.1198	0.1118	0.0992	0.0769	0.0582	0.0299	0.0084				
8*p*	0.1563	0.1433	0.1372	0.1295	0.1198	0.1117	0.0991	0.0767	0.0579	0.0294	0.0078				
8*d*	0.1563	0.1433	0.1371	0.1295	0.1197	0.1116	0.0989	0.0764	0.0573	0.0283	0.0065				
8*f*	0.1563	0.1433	0.1371	0.1294	0.1196	0.1115	0.0986	0.0758	0.0564	0.0268	0.0046				
8*g*	0.1563	0.1433	0.1371	0.1294	0.1195	0.1112	0.0983	0.0751	0.0553	0.0248					
8*h*	0.1563	0.1433	0.1370	0.1293	0.1193	0.1110	0.0978	0.0742	0.0538	0.0221					
8*i*	0.1563	0.1432	0.1370	0.1292	0.1191	0.1107	0.0973	0.0730	0.0520	0.0188					
8*k*	0.1563	0.1432	0.1369	0.1290	0.1189	0.1103	0.0966	0.0716	0.0498	0.0148					
9*s*	0.1235	0.1106	0.1046	0.0972	0.0879	0.0803	0.0687	0.0488	0.0330	0.0117	0.0006				
9*p*	0.1235	0.1106	0.1046	0.0972	0.0879	0.0803	0.0686	0.0486	0.0327	0.0113					
9*d*	0.1235	0.1106	0.1046	0.0972	0.0878	0.0802	0.0684	0.0483	0.0322	0.0106					
9*f*	0.1235	0.1106	0.1046	0.0971	0.0877	0.0800	0.0681	0.0478	0.0314	0.0094					
9*g*	0.1235	0.1106	0.1045	0.0970	0.0876	0.0798	0.0678	0.0471	0.0304	0.0078					
9*h*	0.1235	0.1106	0.1045	0.0969	0.0874	0.0796	0.0674	0.0462	0.0291	0.0058					
9*i*	0.1235	0.1106	0.1044	0.0968	0.0872	0.0792	0.0669	0.0452	0.0275						
9*k*	0.1235	0.1105	0.1044	0.0967	0.0870	0.0789	0.0662	0.0440	0.0256						
9*l*	0.1235	0.1105	0.1043	0.0966	0.0867	0.0785	0.0655	0.0426	0.0233						

[a]Units are rydbergs ×10.

lytic approximation is given by Smith, by expanding the SSCP exponential and solving the resultant perturbation expression term by term. The results of this form are also shown in Fig. 4, in terms of the energy difference relative to the numerical result. As expected, the expansion approximation is considerably less accurate than the unexpanded perturbation result, although the two results approach the numerical result in the limit $DZ/a_0 \to \infty$. The expansion result has a moderate l dependent error. The results of the perturbation approximation are useful in the limit $DZ/a_0 \gg 1$, but for values of $DZ/a_0 < 10^3$, the use of fitting expressions such as those developed by Rouse is clearly indicated.

The numerical solutions demonstrate that in the limit $d \to 0$, which corresponds to $D \to D_0$, the energy of the bound states goes to zero. For all $D < D_0$, the bound state does not exist. A complete tabulation of these critical screening lengths is presented in Table III for the first 45 one-electron eigenstates. For specified n, lower l values have lower D_0 values. The increase of D_0 with increasing l leads to a crossover of levels, or deviation from the unscreened order, at the 5s state. The 5s energy level crosses the 4f slightly above $D_0(5s)Z/a_0 = 12.691$.

Harris[3] also computed values of D_0 for the one-electron SSCP eigenstates using perturbation and variational techniques. These results are within 5–10% of the numerical solution results for the levels $n, l = n-1$. For levels with lower l values, the discrepancies become much larger.

Schey and Schwartz[5] developed a technique for counting the bound states in a short-range central potential and applied this to the SSCP. This method involves the numerical integration of the radial wave equation in the neighborhood of D_0 for each n, l eigenstate, and the isolation of the critical value by monitoring a counting function. It provides an alternative method for computing cutoffs, but offers no particular advantage over the present method for the specific case of the SSCP. Their results for 1s through $n \leq 8$, $l \leq 4$ are very accurate and show excellent agreement with the

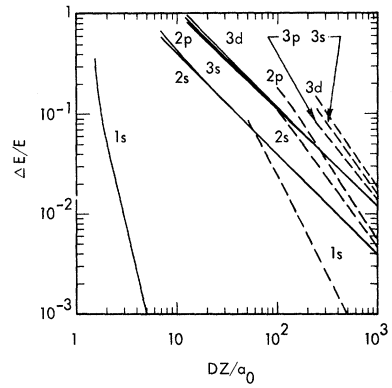

FIG. 4. Error in two approximate expressions for the energy levels given by Smith (Ref. 4) as a function of screening length for some of the lower-lying states. The solid lines give the comparison of the direct perturbation method with the numerical results, while the broken lines represent the approximate expanded perturbation method.

present results. They were able to predict the 5s, 4f crossover and point out the inaccuracies in Harris's cutoff results.

A quantity of special interest is the critical screening length for the ground state of the two-body system in the SSCP, or Yukawa type potential $D_0(1s)$. This parameter has been computed by a variety of techniques. Sachs and Geoppert-Mayer[12] used numerical methods to compute the critical interaction range for the zero-energy deuteron ground state in a Yukawa potential. Hulthén and Laurikainen[13] used a detailed variational calculation to carry out complete solutions for two-particle eigenstates of the Yukawa potential. Lovelace and Masson[14] developed a numerical technique for calculating Regge trajectories, and apply this to the Yukawa potential. They obtain a value for $D_0(1s)$ by interpolating in a set of computed energies for s-wave binding.

The most recent study of the SSCP is that of Iafrate and Mendelsohn,[15] who use both large-Z asymptotic expansion theory and perturbation theory to solve the wave equation for the 1s and 2s states. Their numerical results for the energy eigenvalues as a function of screening agree quite

TABLE III. Critical screening length for one-electron n, l eigenstates, ZD_0/a_0.

n \ l	0	1	2	3	4	5	6	7	8
1	0.8399								
2	3.223	4.541							
3	7.171	8.872	10.947						
4	12.687	14.731	17.210	20.068					
5	19.772	22.130	24.985	28.257	31.904				
6	28.423	31.079	34.285	37.950	42.018	46.458			
7	38.64	41.581	45.122	49.159	53.630	58.500	63.730		
8	50.44	53.641	57.501	61.894	66.752	72.028	77.691	83.720	
9	63.81	67.258	71.426	76.162	81.392	87.064	93.143	99.604	106.43

well with the present study. They have also demonstrated, using a rigorous theorem developed by Schwinger and Bargmann, that there must be a finite number of bound states for the SSCP with finite D.

The plasma theorists have also studied this problem in the SSCP or Debye form. Schey and Schwartz's method gives a value of D_0 for any value of n, l. Harris's value obtained by her best variational approximation is also reasonably accurate. All the foregoing values, together with the result of the present study, are given in Table IV.

The results of Hulthén and Laurikainen, Schey and Schwartz, and the present study are in excellent agreement. The values found by Sachs and Mayer and by Lovelace and Masson are within 1% of the present result.

Examining next the systematic behavior of D_0 (n, l), at first appearance the results are rather complicated. In Fig. 3, the values of D_0 are indicated for all states with cutoff values in the region $50 \leq D_0 Z/a_0 \leq 80$. It can be seen from this segment of D space that the higher value n has the more l-level crossing there is, leading to considerable mixing of the level order. If we examine the dependence of the total number of states n^* which have negative energy at a given D, independent of the unscreened n, l order, a simple and regular relationship is noted. In Fig. 5, the total number of bound states n^* is plotted as a function of the critical screening length. The relation between n^* and D_0 is very close to linear, the deviation being extremely small for $n^* \leq 9$. It should be noted that this same relationship is obtained from the results of Schey and Schwartz,[5] since their D_0 values are the same as those of the present study. If we require the data to fit an equation of the form

$$n^* = a_1 + a_2 DZ/a_0$$

and reduce the data from both studies to form a least-squares fit, the results are those given in Table V. This relation can be used to count the number of states remaining bound at a given value of D, or it may be inverted to compute the value of D_0 for successive values of n^*.

Another quantity of interest is the "maximum

TABLE IV. Critical screening lengths for the 1s state as calculated by various authors.

Source	$D_0(1s)Z/a_0$
Sachs and Mayer (Ref. 12)	0.841 5
Hulthén and Laurikainen (Ref. 13)	0.839 910
Lovelace and Masson (Ref. 14)	0.832 605
Harris (Ref. 3)	0.87
Schey and Schwartz (Ref. 5)	0.840
Present study	0.839 908

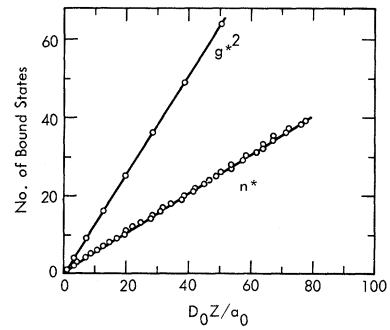

FIG. 5. Number of bound states n^*, and the square of the maximum bound principal quantum number g^*, as a function of the critical screening length D_0.

bound" principal quantum number g^*, or the number of bound s states. The quantity $(g^*)^2$ is also plotted against D in Fig. 5. It exhibits the linear dependence on D that is predicted by theoretical considerations.[1,4] Previous studies have arrived at various values for the slope of this curve. The analytical studies generally give a relationship of the form

$$(g^*)^2 = b_1 DZ/a_0 \ .$$

The numerical studies obtain results which are best fit by a relationship

$$(g^*)^2 = b_2 + b_3 DZ/a_0 \ .$$

The values obtained from the various studies are given in Table V. Although theoretical considerations support the assignment of $b_2 = 0$, the numerical results indicate the existence of the small negative constant. The exact value of the g^*-D relation is no longer as important as previous studies have indicated. The l-dependent and level-mixing behavior of the states renders the use of g^* in a partition function calculation inaccurate. For example, for $D \leq D_0(g^*)$, all states with $n \leq g^*$ would be counted in the sum-over-states if g^* were used to terminate the sum. However, those states with $n = g^*$, $l > 0$ and with $n = g^* - 1$, $l = g^* - 2$, $g^* - 3, \cdots$ (having higher cutoffs than the $n = g^*$, $l = s$ eigenstate) are cut off at higher D values and hence should not be included in the sum.

Throughout this paper, discussion has been restricted to the case of point charges. A more general set of potentials includes a parameter A representing the radius of the interacting charges, as given by Rouse,[6]

$$V(r) = -(Ze^2/r)\,[1 - r(D+A)], \qquad r \leq A$$

$$V(r) = -(Ze^2/r)\,D/(D+A)\,e^{-(r-A)/D}, \qquad r \geq A.$$

The general conclusions given above apply to this form of the potential for $A > 0$ as well as $A = 0$. This is most readily seen by applying the theorem

TABLE V. Fitting coefficients for the number of bound states and the square of the maximum bound principal quantum number as a function of the screening length.

Source	Method	a_1	a_2	b_1	b_2	b_3
Ecker and Weizel (Ref. 1)	analytic approximation			≤ 1		
Kelly and Margenau (Ref. 2)	perturbation			0.86		
Kelly (Ref. 2)	variational			0.804		
Harris (Ref. 3)	perturbation			0.83		
Harris (Ref. 3)	variational			1.30	−0.46	1.38
Smith (Ref. 4)	perturbation			≤ 1		
Schey and Schwartz (Ref. 5)	numerical integration	0.583	0.499	1.267	−0.081	1.269
Present study	numerical integration	0.5829	0.4993	1.2677	−0.1045	1.2701

given by Iafrate and Mendelsohn[15] to this potential. One finds a finite number of states predicted for finite D at all values of A, although the range of physical interest is best restricted to $0 \leq A \leq D$. Although the result one obtains for the critical screening length is only approximate (for $A = 0$ the formula predicts $ZD_0/a_0 = 1$, above the actual value of 0.839 908), if it is adjusted to the correct value one is able to use it to predict D_0 as a function of A. For example, the adjusted formula predicts the D_0/a_0 for the ground state with $A = \frac{1}{2}D$ to be 0.78, while a numerical solution yields 0.77. For $A = D$, the ground state ZD_0/a_0 drops to 0.68.

The disappearance of the bound states under screening reduces not only the number of states but obviously the density of states. Contrary to Rouse's claim that the SSCP has a higher density of states near the continuum than the unscreened potential, the SSCP has a lower density of states for all finite D. While it is true that the separation between n levels is lessened under screening, the concentration of low n levels toward the continuum is more than compensated for by the removal of high-n levels into the continuum. The result is a significantly lower density of states near the continuum in the screened potential. In the limit $D \to \infty$, the density of states of the two potentials (screened and unscreened) becomes equal.

To compute an atomic partition function using the SSCP, the energy eigenvalues and critical screening lengths calculated above are applicable. Jackson and Klein,[7] in a study of these two forms, (2.2a) and (2.2b), find the shifted SSCP to be the better potential for use in hydrogen statistical mechanical calculations. To compute an atomic partition function for the shifted SSCP, one adds to all SSCP energy eigenvalues the term $-e^2/D$.

A different approach to this problem was used by Rouse,[16] who approximated the SSCP atom with its finite number of levels by an atom with an infinite number of levels, using a screening-dependent normalization factor to terminate the sum. That this method leads to approximately equivalent partition functions is a consequence of the existence of the critical values of D. By using standard starting conditions for the numerical integration, choosing some constant for the value of the eigenfunction or its nth derivative at the origin, one finds the unnormalized probability integral increasing as D is increased. This is a result of the screening perturbation, which causes the electronic charge distribution to move farther away from the origin. Thus, the normalization factor must decrease as D decreases from its unscreened value at $D = \infty$ approaching zero as $D \to D_0$. If one then uses the criterion that the level be cut off when the ratio of the screened to the unscreened normalization factor equals some arbitrary small fraction, as a result the level is cut off for some D slightly larger than D_0.

In conclusion, it should be noted that recent studies have questioned the correctness of using either form of the SSCP potential to represent the dynamic screened Coulomb potential, which applies to an atom in a plasma. Jackson and Klein[7] have demonstrated inconsistencies arising from use of SSCP eigenvalues in a hydrogen partition function. Nakayama and DeWitt[17] have found some evidence that the damping effects included in the dynamic potential are of the same order as the level shifts computed from the static potential. A more complete treatment of the screened Coulomb potential would seem to be indicated.

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Spin-Optimized Self-Consistent-Field Function. II. Hyperfine Structure of Atomic Nitrogen

Uzi Kaldor
Department of Chemistry, Tel-Aviv University, Ramat-Aviv, Israel
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The spin-optimized self-consistent-field (SOSCF) method, based on optimizing the spin function in the whole (S, M_s) space simultaneously with spatial orbital optimization, is applied to the ^4S ground state of the nitrogen atom. The maximally paired Hartree-Fock (MPHF) function, where both 1*s* and 2*s* electron pairs are associated with the singlet factor $\alpha\beta - \beta\alpha$, is also calculated, as are functions in which either the 1*s* or the 2*s* electrons are thus paired. The SOSCF energy is −54.421 67 Hartree, compared with −54.400 93 by the restricted Hartree-Fock (RHF) and −54.417 22 by the MPHF methods. The net spin density at the nucleus, responsible for the hfs of nitrogen, is 0.1200 a.u., compared with 0.1853 a.u. by the spin-extended Hartree-Fock method and the experimental value of 0.0972 a.u. (the RHF and MPHF methods give 0). The contributions of the 1*s* and 2*s* pairs, obtained from two separate calculations employing two-dimensional subspaces of the six-dimensional spin-function space, add very nearly to the full SOSCF results for the energy and spin density. The SOSCF orbitals are also described. Their most interesting feature is the nonexistence of radial nodes in any of them.

INTRODUCTION

The spin-optimized self-consistent-field (SOSCF) function described in a recent paper[1] is of the form

$$\Psi = \mathcal{A}\Xi\Theta \quad , \tag{1}$$

where Ξ is a product of one-electron spatial functions

$$\Xi = \chi_1(1)\chi_2(2)\cdots\chi_n(n) \quad , \tag{2}$$

and Θ is a linear combination of all independent spin functions θ_k spanning the space of appropriate S and M_s

$$\Theta = \sum_k t_k\theta_k \quad . \tag{3}$$

The orbitals χ_i and the coefficients t_k are optimized to obtain the SOSCF function. Similar methods have been recently described by other authors.[2] The SOGI function of Ladner and Goddard[2a] is equivalent to our SOSCF function, though obtained in a different way. The BRNO method[2b] is somewhat inferior, not involving reoptimization of the spatial orbitals for the best spin function.

In paper I,[1] we investigated three- and four-electron atoms. These systems have only two independent spin functions [$k = 1$, 2 in Eq. (3)], and the optimal Θ is found to be very close to θ_1, the maximally paired Hartree-Fock function (MP HF, equivalent to Goddard's G1[3]), with a singlet factor of $\alpha\beta - \beta\alpha$ corresponding to the two 1*s* electrons (and to the 2*s* electrons in Be). The contribution of the other function t_2 is two orders